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# The impact of alkenone degradation on $U_{37}^{K'}$ paleothermometry: a model-derived assessment

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### Key Points:

- Reaction-Transport modelling shows that selective degradation of alkenones can positively bias SST records
- SST records are only likely to be affected if alkenones experience extensive degradation during burial
- The majority of alkenone-based SST records are unlikely to be affected by post-burial selective degradation

## Abstract

The  $U_{37}^{K'}$  proxy for past sea surface temperature (SST) is based on the unsaturation ratio of  $C_{37}$  alkenones. It is considered a diagenetically robust proxy, but biases have been invoked because the index can be altered by preferential degradation of the  $C_{37:3}$  alkenone, resulting in higher reconstructed SST. However, alkenone degradation rate constants are poorly constrained, making it difficult to evaluate the plausibility of such a bias. Therefore, we quantitatively assessed the effect of: (1) different alkenone degradation rate constants; (2) differential degradation factors between di- and tri-unsaturated  $C_{37}$  alkenones; (3) and initial  $U_{37}^{K'}$  values on the  $U_{37}^{K'}$  paleothermometer for two depositional environments (shelf and upper-slope), by means of a Reaction-Transport Model (RTM). RTM results reveal that preferential degradation of  $C_{37:3}$  can potentially alter the original signal of the  $U_{37}^{K'}$  paleothermometer, but SST biases ( $\Delta$ SST) are largely within  $U_{37}^{K'}$  calibration error ( $\Delta$ SST < 1.5 °C) assuming realistic model parameters. The magnitude of  $\Delta$ SST is largely determined by the degradation rate constant, but it also increases with higher differential degradation factors. Additionally, initial  $U_{37}^{K'}$  values exert a non-linear influence on the extent of potential SST bias, with mid-range values (0.4 <  $U_{37}^{K'} < 0.6$ ) being most sensitive. The most significant changes occur in the shallowest sediment layers and are attenuated with burial time/depth. Scenarios where  $\Delta$ SST > 1.5 °C are associated with marked downcore decreases in alkenone concentration. Consequently, we caution against the interpretation of  $U_{37}^{K'}$  indices when extensive degradation results in very low alkenone concentrations (< 5 ng g<sup>-1</sup>).

*Key-words:* Sea surface temperature; reaction-transport model; paleoceanography; paleoclimate;  $U_{37}^{K'}$  paleothermometer, preferential degradation.

## 1 Introduction

Alkenones are long chain unsaturated ketones (C<sub>36</sub>-C<sub>39</sub>; di-, tri-, or tetra-unsaturated) that were first detected in marine sediments by *Boon et al.* [1978] and then systematically identified by *de Leeuw et al.* [1980] and *Volkman et al.* [1980b]. In the present day ocean, the modern biological precursor of these compounds are reticulofenestrid haptophytes, such as *Emiliana huxleyi* and *Gephyrocapsa oceanica* [Volkman et al., 1980a, 1980b, 1995; Marlowe et al., 1990; Conte and Eglinton, 1993; Volkman, 2000]. Although the occurrence of alkenones extends to the Cretaceous period [Farrimond et al., 1986; Brassell and Dumitrescu, 2004], the presence of alkenones in Cretaceous sediments is uncommon and restricted to di-unsaturated alkenones, possibly because the C<sub>37:3</sub> metabolic pathway only developed in response to long-term global cooling [Brassell, 2014]. The oldest observed tri-unsaturated alkenones occur in early Eocene sediments, but even then they are relatively uncommon [Marlowe et al., 1984; Weller and Stein, 2008; Brassell, 2014].

Crucially, numerous studies have revealed a relationship between the degree of unsaturation of C<sub>37</sub> alkenones (C<sub>37:2</sub>, C<sub>37:3</sub>, and C<sub>37:4</sub>; Figure 1) and algae growth temperature, resulting in the development of the U<sub>37</sub><sup>K</sup> index as a proxy for sea surface temperature [Brassell et al., 1986]. However, because C<sub>37:4</sub> alkenone concentrations are typically low (or zero) [Grimalt et al., 2000] and display a high variability in relative abundance and geographic distribution across ocean basins, as well as a poor correlation with SST [Rosell-Melé et al., 1994; Sikes et al., 1997; Sikes and Sicre, 2002; Bendle and Rosell-Melé, 2004], Prahl and Wakeham [1987] and Prahl et al. [1988] proposed the now more widely used U<sub>37</sub><sup>K'</sup> (Eq. 1) index based on the concentrations of C<sub>37:3</sub> and C<sub>37:2</sub> alkenones:

$$U_{37}^{K'} = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]} \quad (\text{Equation 1}).$$

69 The quantitative relationship between the  $U_{37}^{K'}$  index and ambient growth temperature has been  
70 calibrated on the basis of laboratory cultures, as well as on suspended particulate organic matter  
71 and sediment coretops [Prahl and Wakeham, 1987; Müller et al., 1998].

72 Alkenones are usually well preserved in the sedimentary record [Sikes et al., 1991;  
73 Prahl et al., 2000]. As such, the  $U_{37}^{K'}$  paleothermometer is considered diagenetically robust (*i.e.*  
74 resistant and/or little altered during diagenesis) and is extensively used to reconstruct past  
75 ocean and lake surface temperature [Prahl et al., 2000, 2003; Ho et al., 2013; Brassell, 2014].  
76 Consequently, the validity of the proxy relies on the assumptions that alkenones are relatively  
77 recalcitrant and, more importantly, that all  $C_{37}$  alkenones degrade at similar rates. However,  
78 several studies have shown that alkenones can be rapidly degraded in the water column, in  
79 marine sediments, and under laboratory conditions [Conte et al., 1992; Freeman and Wakeham,  
80 1992; Hoefs et al., 1998; Teece et al., 1998; Gong and Hollander, 1999; Rontani et al., 2005,  
81 2008; Rontani and Wakeham, 2008; Huguet et al., 2009]. In addition, unsaturated lipids are  
82 generally considered more easily degradable than saturated compounds [Volkman et al., 1983;  
83 Cranwell et al., 1987; Grimalt et al., 2000], and different alkenones might thus be degraded at  
84 different rates.

85 However, there is conflicting evidence regarding the question whether there is a  
86 preferential degradation of  $C_{37:3}$  over  $C_{37:2}$  alkenones. Several studies found no evidence for  
87 preferential degradation [*e.g.*, Prahl et al. 1989, 2000, 2003; Sikes et al. 1991; Conte et al.  
88 1992; Rontani et al. 1997; Teece et al. 1998; Grimalt et al. 2000; Herbert, 2001], whereas  
89 others directly observed or inferred a higher degradation of the  $C_{37:3}$  alkenone [Freeman and  
90 Wakeham, 1992; Hoefs et al., 1998; Gong and Hollander, 1999; Rontani et al., 2005, 2008,  
91 2013; Huguet et al., 2009]. Their observations indicate that the potential bias in reconstructed  
92 SST induced by such a preferential degradation ranges from 0 to up to +5.9 °C under both oxic  
93 and anoxic conditions and in both in the water column and sediments [Rontani et al., 2013].

94           Regardless of the main drivers of preferential degradation, a potential diagenetic  
95   modification of the primary signal could have important implications for paleoreconstructions  
96   and could result in erroneous conclusions. For instance, many Paleogene sediments only  
97   contain the C<sub>37:2</sub> alkenone [*e.g.*, Marlowe *et al.* 1984; Pagani *et al.*, 1999, 2000; Mercer and  
98   Zhao, 2004; Lyle *et al.*, 2006]. These observations could be interpreted as a high SST during  
99   the Paleogene or could be the result of preferential degradation of the C<sub>37:3</sub> alkenone. Much of  
100   the scientific debate has revolved around the existence of preferential degradation and its  
101   potential controls, whereas little attention has been devoted to quantitatively assessing the  
102   potential influence of preferential degradation on the downcore profiles of C<sub>37:2</sub> and C<sub>37:3</sub> and  
103   thus, the evolution of the U<sub>37</sub><sup>K'</sup> ratio during burial. Such an assessment would not only advance  
104   our understanding of the possible impacts of preferential degradation on the U<sub>37</sub><sup>K'</sup> derived  
105   paleoreconstructions, but could also help identify the range of conditions (*e.g.* sedimentation  
106   rate, concentrations, degradation rate constants) under which preferential degradation could  
107   compromise the applicability of the U<sub>37</sub><sup>K'</sup> paleothermometer. Furthermore, it could help  
108   disentangle the interplay between preferential degradation and additional processes that can  
109   induce SST biases, such as resuspension and lateral transport [*e.g.*, Benthien and Müller, 2000;  
110   Ohkouchi *et al.*, 2002; Mollenhauer *et al.*, 2003].

111           However, alkenone degradation rate constants are poorly constrained, making it  
112   difficult to quantitatively assess the influence of preferential degradation on U<sub>37</sub><sup>K'</sup> derived  
113   paleoreconstructions. In addition, extrapolating experimental results of alkenone degradation  
114   to geological timescales, especially over a large range of environmental conditions, is not  
115   straightforward. Therefore, here we use a reaction-transport model (RTM) approach [Berner,  
116   1980; Boudreau, 1997] to quantitatively assess the potential impact of preferential degradation  
117   on the U<sub>37</sub><sup>K'</sup> paleothermometer during burial in marine sediments. The specific aims of this work  
118   are to: (1) quantitatively assess the impact of preferential degradation on U<sub>37</sub><sup>K'</sup>

paleothermometry; (2) identify the main factors that control SST biases and quantify their relative significance; and (3) based on the model results, evaluate the impact of preferential degradation on the application of the  $U_{37}^{K'}$  paleothermometer. With respect to the latter, we revisit previously published data but our goal is not to recalculate published SSTs; rather it is to explore the implications of our sensitivity experiment for such records and provide a guide for critical assessment of the  $U_{37}^{K'}$  proxy in future studies.

## 2 Model Description

The RTM approach allows the simultaneous tracking of alkenone concentrations and the sedimentary  $U_{37}^{K'}$  indices in a given sediment layer during burial in marine sediments. Additionally, model simulations enable an evaluation and comparison of short- and long-term impacts. Here, we first provide a detailed description of the modelling approach. The model is then used to explore the evolution of the  $U_{37}^{K'}$  ratio during burial for different environmental conditions (depositional environments with distinct sediment accumulation rates and bioturbation coefficients),  $U_{37}^{K'}$  initial values, and alkenone degradation parameters (degradation rate constant and differential degradation factor between alkenones). We develop a comprehensive sensitivity study that allows us to explore the full range of these parameters, given their poorly constrained nature, in order to establish a quantitative framework for understanding the conditions under which  $U_{37}^{K'}$  indices could have been biased. The model developed here is based on the vertically-resolved mass conservation equation for alkenones in marine sediments (Eq. 2) [*e.g.*, Berner, 1980]:

$$\frac{\partial C_{37:i}}{\partial t} = - \frac{\partial F_i}{\partial z} + \sum_j R_i^j \quad (\text{Equation 2}),$$

where  $C_{37:i}$  is the concentration of alkenone  $i$ ,  $z$  is the sediment depth,  $t$  denotes the time,  $F_i$  summarizes the advective and dispersive flux divergence of alkenone  $i$  and  $\sum_j R_i^j$  represents

the sum of production/consumption rates  $j$  that affect alkenone  $i$ . This approach allows the evolution of alkenone concentration to be explored with both burial time and burial depths. Burial depth and time are directly linked via the characteristic timescales of transport processes  $F_i$  (*i.e.* in a non-compacting sediment, burial time  $t=z/w$ ). Figure 2 shows a conceptual illustration of the alkenone degradation model applied here and the following sections provide a detailed model description.

The model accounts for the advective burial flux of alkenones, as well as the random displacement of sediments caused by the activity of infaunal organisms in the bioturbated zone of the sediment ( $z < z_{bio}$ ), which is described as a dispersive process [Boudreau, 1986] with a constant bioturbation coefficient  $D_{bio}$ . The bioturbation coefficient is set to zero below the bioturbated zone. In addition, alkenones are consumed by heterotrophic degradation during burial. The degradation of organic compounds is a multi-step process. However, the initial hydrolysis step is considered to be the rate limiting step and the degradation process is thus generally described as a single step reaction following first order kinetics [*e.g.*, Arnosti, 2011]. Traditionally, organic matter reactivity and thus, the reaction rate constant or reactivity,  $k$ , of the kinetic rate law is assumed to be controlled by the molecular structure of the organic compound [*e.g.*, Rechka and Maxwell, 1988; Sun and Wakeham, 1994]. In this case, the susceptibility of alkenone  $C_{37:i}$  towards microbial degradation would not change during burial and its degradation can thus be described by a constant reactivity  $k_i$ . The resulting rate law is equivalent to the so-called 1G Model [*e.g.*, Boudreau 1997]. However, some empirically determined  $k_i$  values from pelagic environments and shallow oxic sediments are extremely high. For instance, Gong and Hollander [1999] determined rate constants of  $k_i \approx 10^{-3} \text{ yr}^{-1}$  for sediments from the Santa Monica Basin, and Freeman and Wakeham [1992] and Sun and Wakeham [1994] measured a value of  $k_i = 9.0 \cdot 10^{-3} \text{ yr}^{-1}$  in sediments from the Black Sea. If applied in a 1G model, such high rate constants would result in a complete alkenone



consumption within the upper sediment layer and thus, contradict the observed persistence of alkenones in marine sediments, suggesting that these rate constants are not representative or that alkenone reactivity might decrease with depth/time. Indeed, observations have shown that the reactivity of organic matter is not only controlled by its chemical structure. Organic matter reactivity results from the interplay between the organic matter and its environment, and consequently is not a characteristic attributed solely to organic matter itself [Mayer, 1995]. Therefore, the reactivity of the C<sub>37</sub> alkenones could, in addition to their molecular structures, also be controlled by factors such as the macromolecular structure in which the compounds are incorporated, oxygen exposure time and terminal electron acceptor availability, microbial community structure, physical protection, and priming [e.g., Aller, 1994; Keil *et al.*, 2004; Burdige, 2006; Zonneveld *et al.*, 2010; Arndt *et al.*, 2013]. In fact, observational evidence indicates that the degradation of lipids, amino acids, carbohydrates, as well as of bulk organic carbon is more similar within a depositional setting than the degradation of individual compounds across sites [e.g., Burdige, 2006]. This suggests that alkenones degrade similarly as bulk organic matter and that additional environmental controls could cause a decrease in apparent alkenone reactivity during burial. Several studies support this hypothesis. They show that additional factors, such as oxygen exposure times [e.g., Gong and Hollander, 1999] and microbial community dynamics [e.g., Rontani *et al.*, 2008], can exert an influence on the apparent reactivity of alkenones, causing  $k$  to decrease during burial. Such a decrease in reactivity can be mathematically described by a power law, equivalent to the widely used reactive continuum (RCM) and power models of organic matter degradation [Middelburg, 1989; Boudreau and Ruddick, 1991]. Here, we developed two reactivity scenarios to test the influence of preferential degradation on changes in SST assuming (1) a constant alkenone reactivity with burial depth (1G model), based on the classical view of a chemical structure controlled degradation, and (2) a decreasing alkenone reactivity with burial depth (power

model/reactive continuum model), based on observational evidence for additional controls on apparent alkenone reactivity.

*Scenario 1: Constant reactivity,  $k_i$ , during burial (1G model) (Eq. 3-4):*

Assuming a constant reactivity,  $k_i$ , the vertically-resolved mass conservation equation for alkenone concentrations,  $C_{37:i}$ , in marine sediments can be formulated as:

$$\frac{\partial C_{37:i}}{\partial t} = D_{bio} \frac{\partial^2 C_{37:i}}{\partial z^2} + \omega \frac{\partial C_{37:i}}{\partial z} - k_i C_{37:i} \text{ for } z < z_{bio} \text{ (Equation 3)}$$

$$\frac{\partial C_{37:i}}{\partial t} = \omega \frac{\partial C_{37:i}}{\partial z} - k_i C_{37:i} \text{ for } z \geq z_{bio} \text{ (Equation 4),}$$

where  $C_{37:i}$  represents the alkenone ( $C_{37:2}$  or  $C_{37:3}$ ) concentration at depth,  $D_{bio}$  denotes the bioturbation diffusion coefficient,  $\omega$  is the burial velocity, and  $k_i$  is the first order degradation rate constant for alkenone  $C_{37:i}$ . A preferential degradation factor  $f_{C_{37:3}}$  relates the degradation rate constants  $k_i$  of  $C_{37:3}$  and  $C_{37:2}$  alkenones and thus, serves as a quantitative measure of the extent of preferential degradation:

$$k_{37:3} = f_{C_{37:3}} \cdot k_{37:2} \text{ (Equation 5).}$$

*Scenario 2: Decreasing reactivity,  $k_i(z)$ , during burial (Reactive Continuum Scenario) (Eq. 6-7):*

A decrease in alkenone reactivity during burial can be mathematically described by a power law and is equivalent to the widely used reactive continuum (RCM) and power models of organic matter degradation [Middelburg, 1989; Boudreau and Ruddick, 1991]. Assuming a decreasing reactivity,  $k_i(z)$ , the vertically-resolved mass conservation equation for alkenone concentrations,  $C_{37:i}$ , in marine sediments is then given by:

$$\frac{\partial C_{37:i}}{\partial t} = D_{bio} \frac{\partial^2 C_{37:i}}{\partial z^2} + \omega \frac{\partial C_{37:i}}{\partial z} - k_i(z) C_{37:i} \text{ for } z < z_{bio} \text{ (Equation 6)}$$

$$\frac{\partial C_{37:i}}{\partial t} = \omega \frac{\partial C_{37:i}}{\partial z} - k_i(z) C_{37:i} \text{ for } z \geq z_{bio} \text{ (Equation 7),}$$

where the decrease in  $k_i(z)$  with sediment burial age, *burial time*( $z$ ), is described in the form of the power law relationship [Middelburg, 1989; Boudreau and Ruddick, 1991]:

$$k_i(z) = \frac{p_i}{a_i + \text{burial time}(z)} \text{ (Equation 8),}$$

where  $p_i$  and  $a_i$  are parameters that determine the depth profile of  $k_i$ . The  $a_i$  parameter denotes the apparent initial age of the alkenone mixture in the sediment and can be seen as a shape parameter, whereas the  $p_i$  parameter scales the initial distribution of alkenones [Boudreau and Ruddick, 1991]. Low  $a_i$  and high  $p_i$  represent a dominance of more bioavailable alkenones, whereas high  $a_i$  and low  $p_i$  represent a dominance of less bioavailable alkenones. Therefore, the apparent alkenone reactivity in the upper sediment layers will be higher for low  $a_i$  values (more bioavailable alkenones), which results in a rapid loss of alkenones at surface sediments, but also a rapid decrease in  $k_i(z)$  with depth. Alternatively, high  $a_i$  values will yield lower apparent alkenone reactivity close to the sediment-water interface (less bioavailable alkenones); consequently, alkenones will have lower degradability at surface sediments and the downcore decrease in  $k_i(z)$  will be slower [see Arndt *et al.*, 2013 Fig. 10 for details]. In the case of the RCM, the preferential degradation factor  $f_{C37:3}$  could in theory be applied to both the  $a_i$  and  $p_i$  parameter. The parameter  $p_i$  merely scales the reactivity of alkenones. The application of the preferential degradation factor  $f_{C37:3}$  to  $p_i$  according to

$$p_{37:3} = f_{C37:3} \cdot p_{37:2} \text{ (Equation 9)}$$

results in a shift of the entire reactivity profile  $k_i(z)$  for tri-saturated alkenones to higher reactivity and is identical to its use in Scenario 1. It is important to note that, in this case, the 1G model represents an end-member RCM scenario, *i.e.* no decrease of alkenone reactivity with burial time/depth and therefore, can be considered as a ‘worst case’ scenario for a preferential degradation bias.

We can further assume a different decrease in reactivity with burial between the two alkenones. In this case, a preferential degradation arises from a difference in  $a_i$  values ( $C_{37:3}$  more labile than  $C_{37:2}$ , *i.e.*  $a_{37:3} \ll a_{37:2}$ ) and, thus, the preferential degradation factor would be applied to  $a_i$ . Such assumption, however, would suggest that the two alkenones have distinct sources, undergo different transport mechanisms, and/or are differently affected by mineral protection, microbial community dynamics or terminal electron acceptor availability before/during burial. Those assumptions seem unlikely, and if true, would prevent the application of  $U_{37}^{K'}$  as a SST proxy. Therefore, we generally assume that the parameter  $a_i$ , which controls the shape of the reactivity decrease with depth, is identical for both alkenones. Nonetheless, we also tested this hypothesis to assess the potential SST biases that could arise from such conditions.

## 2.1 Solution

Equations 3-4 and 6-7 can be used to trace the evolution of alkenone concentrations in a given sediment layer during burial by assuming steady state conditions ( $\frac{\partial C}{\partial t} = 0$ ) and a constant porosity, thus neglecting sediment compaction. In addition, we also assume that benthic activity efficiently mixes material in the bioturbated layer, resulting in a constant age. Burial time (*i.e.* the age of a given sediment layer) and burial depth,  $z$ , are then related by:

$$\text{burial time}(z) = 0 \text{ for } z < z_{bio} \text{ (Equation 10),}$$

$$\text{burial time}(z) = \frac{z - z_{bio}}{\omega} \text{ for } z \geq z_{bio} \text{ (Equation 11).}$$

The integration of Eqs. 3-4 and 6-7 can then be solved analytically and yield the following general solutions representing the evolution of alkenone concentrations with burial depth/time:

Scenario 1: Constant reactivity,  $k_i$ , during burial (1G Scenario) (Eq. 3-4):

$$C_{37:i}(z) = A_1 e^{a_1 \cdot z} + B_1 e^{b_1 \cdot z} \text{ for } z < z_{bio} \text{ (Equation 12)}$$

$$C_{37:i}(z) = A_2 e^{a_2 \cdot z} \text{ for } z \geq z_{bio} \text{ (Equation 13)}$$

where:

$$a_1 = \frac{\omega - \sqrt{\omega^2 + 4 \cdot D_{bio} \cdot k_i}}{2 \cdot D_{bio}} \text{ (Equation 14)}$$

$$b_1 = \frac{\omega + \sqrt{\omega^2 + 4 \cdot D_{bio} \cdot k_i}}{2 \cdot D_{bio}} \text{ (Equation 15)}$$

$$a_2 = \frac{-k_i}{\omega} \text{ (Equation 16)}$$

Determining the integration constants  $A_1$ ,  $B_1$  and  $A_2$  requires the definition of boundary conditions. Here, we assume:

(1) a known concentration of the alkenones at the sediment water interface

$$C_{37:i}(0) = C_{37:i,0} \text{ (Equation 17);}$$

and (2 and 3) continuity between the bioturbated and non-bioturbated zone:

$$(2) C_{37:i,1}(z_{bio}) = C_{37:i,2}(z_{bio}) \text{ (Equation 18);}$$

$$(3) D_{bio} \cdot \frac{\partial C_{37:i}}{\partial z} |_{z_{bio}} = 0 \text{ (Equation 19).}$$

Scenario 2: Decreasing reactivity,  $k_i(z)$ , during burial (Eq. 5-6; RCM Scenario):

$$C_{37:i}(z) = A_1 e^{a_1 \cdot z} + B_1 e^{b_1 \cdot z} \text{ for } z < z_{bio} \text{ (Equation 20)}$$

$$C_{37:i}(z) = C_{37:i}(z_{bio}) \cdot \left( \frac{a_i}{a_i + \text{burial time}(z)} \right)^{-p_i} \text{ for } z \geq z_{bio} \text{ (Equation 21)}$$

where:

$$a_1 = \frac{\omega - \sqrt{\omega^2 + 4 \cdot D_{bio} \cdot p_i / a_i}}{2 \cdot D_{bio}} \text{ (Equation 22)}$$

$$b_1 = \frac{\omega + \sqrt{\omega^2 + 4 \cdot D_{bio} \cdot p_i / a_i}}{2 \cdot D_{bio}} \text{ (Equation 23)}$$

Eq. 6 is thus mathematically equivalent to Eq. 3 with reactivity  $k_i(z) = p_i/a_i$  (Equation 24), within the bioturbated layer.

Determining the integration constants A1, B1 requires the definition of boundary conditions. Here, we assume:

(1) a known alkenone concentration at the sediment water interface

$$C_{37:i}(0) = C_{37:i,0} \text{ (Equation 25);}$$

(2) continuity between the bioturbated and non-bioturbated zone:

$$(2) D_{bio} \cdot \frac{\partial C_{z_{bio}}}{\partial z} |_{z_{bio}} = 0 \text{ (Equation 26).}$$

## 2.2 Model Parameters and Boundary Conditions

Model parameters and boundary conditions place the model in its environmental context. Table 1 provides an overview of the respective model parameters and boundary conditions, their units and their values. Model parameters can be divided into those that define the general depositional environment and are generally well constrained, and those that control alkenone degradation and are generally variable and/or poorly constrained. Therefore, a two-step sensitivity study is conducted here. Model simulations are carried out for two different depositional environments (coastal sediments – water depth 200 meters; and upper slope sediments – water depth 1000 meters) to explore their potential impact on preferential degradation and the  $U_{37}^{K'}$  paleothermometer. In addition, for each depositional setting, a sensitivity study is conducted over the entire range of plausible degradation parameters to account for the parameter uncertainty of degradation parameters.

### 2.2.1 Sensitivity to Depositional Environment

In marine sediments, burial depth and time are directly linked via the characteristic timescales of transport processes (Eq. 10-11) and, thus, the bioturbation coefficient, bioturbation depth and burial velocity. The model calculates the alkenone concentration depth profiles for both a typical coastal sediment, as well as an upper slope sediment up to a maximum sediment column depth of 250 meters.

Based on a compilation of mixing layer depths [Boudreau, 1994, 1998], the depth of the bioturbated zone is set to 10 cm for both water depth scenarios. Bioturbation coefficients and burial velocities are determined based on a water depth dependent relationship proposed by Middelburg *et al.* [1997]. This approach aims at providing a general framework for potential alkenone bias with burial time/depth for contrasting depositional environments rather than simulating any specific setting. Note that, since the model traces the evolution of alkenone layers during burial, (likely) changes in sedimentation rate over burial time would merely have an impact on the calculation of burial depth (Eq. 11). For instance, a decrease in sedimentation rate would simply reduce burial depth for a given burial time, but would not have an impact on the simulated SST bias and, thus, the overall results. Although C<sub>37</sub> alkenone concentrations at the sediment water interface (SWI) can be highly variable depending on local primary production rates and vertical transport in the water column, sediment trap and surface sediment studies [Gong and Hollander, 1999; Müller and Fischer, 2001; Prahl *et al.*, 2001; Rodrigo-Gámiz *et al.*, 2016] indicate that alkenone concentrations in settling suspended matter and surface sediments typically range from approx. 4 – 77 µg g<sup>-1</sup>. Thus, the total C<sub>37</sub> alkenone (C<sub>37:2</sub> + C<sub>37:3</sub>) concentration at the SWI was set to 5 µg g<sup>-1</sup>.

### 2.2.2 Sensitivity to Uncertainty in Degradation Rate Parameters

Most of the parameters that control the potential degree of preferential degradation (such as the initial  $U_{37}^{K'}$  of the material that has been deposited at SWI,  $U_{37}^{K'}(0)$ ; the degradation rate constant,  $k_i$ ; and the differential degradation factor between di- and tri-unsaturated  $C_{37}$  alkenones,  $f_{C37:3}$ ) are either variable and/or difficult to constrain. Therefore, we designed a comprehensive parameter sensitivity study in order to assess the response of alkenone concentration depth profiles and thus, the  $U_{37}^{K'}$  ratio to different degrees of preferential degradation. The evolution of alkenone concentrations with burial time/depth is thus simulated over the entire plausible parameter range of: i) the initial  $U_{37}^{K'}$ ,  $U_{37}^{K'}(0)$ ; ii) the degradation rate constant,  $k_i$ ; and iii) the differential degradation factor between di- and tri-unsaturated  $C_{37}$  alkenones,  $f_{C37:3}$ .

The  $U_{37}^{K'}(0)$  was varied over the entire range of 0.1 to 0.9  $U_{37}^{K'}$  units only excluding  $U_{37}^{K'} = 0$  and  $U_{37}^{K'} = 1$ , reflecting the absence of  $C_{37:2}$  and  $C_{37:3}$ , respectively. Degradation rate constants,  $k_i$ , are notoriously difficult to constrain. First order rate constants derived from laboratory experiments [Teece *et al.*, 1998] are often not directly transferable to marine sediments characterized by low or no oxygen exposure, low temperature and high pressure [Schouten *et al.*, 2010] and estimates from the field are highly variable [*e.g.*, Sun and Wakeham, 1994; Gong and Hollander, 1999]. Therefore, we do not rely on these rate constant values; instead, we explore the entire range of potential values. However, we do interpret the model results in the context of these experimental and field estimates (see *Section 4.1*). Model-derived first-order degradation rate constants of bulk organic matter typically vary by several orders of magnitude, from as high as  $10^1 \text{ yr}^{-1}$  to as low as  $10^{-9} \text{ yr}^{-1}$  [Arndt *et al.*, 2013]. Therefore, we vary the first order degradation rate constant  $k_i$  from  $10^{-5}$  to  $10^{-3} \text{ yr}^{-1}$  (1G model). The lower limit is set to  $10^{-5} \text{ yr}^{-1}$ , because lower degradation rate constants result in a negligible effect of preferential degradation on  $U_{37}^{K'}$ ; as such, this study represents a ‘worst case scenario’ for  $U_{37}^{K'}$



bias. The upper limit is defined as  $10^{-3} \text{ yr}^{-1}$ , because levels higher than that seem unrealistic, since they result in complete consumption of alkenones in the sediment surface layer.

Similar to constant first order degradation rate constants, the free parameters  $p$  and  $a$  that control the shape of the  $k_i(z)$  depth profile are also difficult to constrain. Model-derived parameters from a wide range of different environments indicate that  $p$  generally falls within the range between  $10^{-2}$  and  $10^0$ , while the parameter  $a$  may vary over several orders of magnitude from  $10^{-1}$  to  $10^6$  yrs [Arndt *et al.*, 2013]. Here, the free parameter  $a_i$  varies from  $10^{-1}$  to  $10^4$  yrs, whereas  $p_i$  varies from  $10^{-2}$  to  $10^0$ . We, therefore, explore the entire range of plausible degradation rate constants for both the 1G model and the RCM scenario.

To simulate the preferential degradation of tri-unsaturated alkenones, a ratio between the  $C_{37:3}$  degradation rate constant and the  $C_{37:2}$  degradation rate constant – a preferential degradation factor  $f_{C_{37:3}}$  – is defined and varied from 1.1 to 1.5 (*i.e.*  $C_{37:3}$  degradation is 10% to 50% faster than the degradation of  $C_{37:2}$ ). This range has been informed by observed differences of preferential alkenones degradation in field and laboratory experiments [*e.g.*, Hoefs *et al.*, 1998; Gong and Hollander, 1999; Rontani *et al.*, 2005, 2008].

### 2.3 Model Output

The model calculates the evolution of individual alkenone concentrations over burial time/depth (Eq. 3-4 and 6-7). Based on these simulated concentrations,  $U_{37}^{K'}$  ratios are calculated according to Eq. 1. SSTs are estimated based on the calculated  $U_{37}^{K'}$  ratios using the global core-top calibration of Müller *et al.* [1998] (Table 1). SST is calculated from the SWI down to 250 meter below sea floor (mbsf) for the parameter combinations described in Table 1. The deviation of the estimated SST from the original SST recorded by the material deposited at the sediment-water interface or, in other words, the SST bias due to preferential degradation ( $\Delta\text{SST}$ ; Table 1) is calculated for typical burial depths 50, 100, 150, 200, and 250 mbsf. For

the hypothetical coastal sediments (200 meters depth), those depths represent burial times of approximately 14 kyr, 28 kyr, 42 kyr, 55 kyr, and 70 kyr, respectively. For the hypothetical upper slope sediments (1000 meters depth), those depths correspond to 31 kyr, 62 kyr, 94 kyr, 125 kyr, and 156 kyr, respectively.

### 3 Results

In the following sections, we mainly focus on the findings derived from the 1G approach (Figures 3 – 6; Table 2) or, in other words, the ‘worst case’ endmember RCM scenario (negligible decrease in  $k_i$  with depth/time) described in Section 2.2. We do so because that approach results in the most extensive degradation and, thus, SST bias. As such, simulation results will help to delineate a conservative range of conditions that favor preferential degradation and potentially result in SST bias. The discussion of the 1G – ‘worst case’ RCM – simulation results are supplemented with simulation results from Scenario 2 (Figures 7 – 10), in which we test a broad range of  $a_i$  and  $p_i$  values.

Figures 3 to 6 summarize changes in the  $U_{37}^{K'}$  derived SSTs and alkenone concentrations as a function of all parameters explored in the Scenario 1. To illustrate the effect of preferential degradation on  $\Delta$ SST (*i.e.* the deviation from the real SST) for a wide range of degradation scenarios and environmental conditions, interpolated plots of simulated  $\Delta$ SST over the simulated  $U_{37}^{K'}(0)$  and  $f_{C37:3}$  space are produced for each water depth (Fig. 3-6 a and b, two columns: 200 m and 1000 m), different burial depths/times (Fig. 3-6 a and b, 5 panels per column: 50 mbsf, 100 mbsf, 150 mbsf, 200 mbsf and 250 mbsf), and degradation rate constants (Fig. 3-6). The simulated burial depths represent sediment ages ranging from 14 kyr to 70 kyr and from 31 kyr to 156 kyr for the shallow and deep site, respectively. In addition, vertical profiles of the preserved fraction of the original deposited total alkenone ( $C_{37:2}+C_{37:3}$ ) concentration over burial depth/time are plotted to visualize the decrease in total alkenone

concentrations (Fig. 3-6 c and d). Furthermore, Table 2 summarizes the range of  $\Delta$ SST values and C<sub>37</sub> alkenone extent of degradation throughout all scenarios explored in Scenario 1.

The 1G simulations (Fig. 3-6) show that the impact of preferential degradation on  $U_{37}^{K'}$  ratios and, thus, the positive bias in reconstructed SST ranges from less than 0.1 °C in the least reactive and/or least selective degradation scenario ( $k_{37:2} = 1.0 \cdot 10^{-5} \text{ yr}^{-1}$ ;  $f_{C37:3} = 1.1$ ;  $U_{37}^{K'}(0) = 0.1$  and 0.9) up to 27 °C in the most extreme ( $k_{37:2} > 1.0 \cdot 10^{-4} \text{ yr}^{-1}$ ;  $f_{C37:3} > 1.4$ ;  $U_{37}^{K'}(0) = 0.1$ ), albeit unrealistic (see below), scenario (Table 2; Figures 3 to 6). In general, the influence of preferential degradation on the bias in reconstructed SST is controlled by a combination of factors. The most important factors are the degradation rate constants  $k_i$ , the initial  $U_{37}^{K'}(0)$  value and the preferential degradation factor  $f_{C37:3}$ , while water depth (and thus, the general depositional environment) exerts an important but subordinate impact. In addition, the lower panels c and d (Fig. 3-6) illustrate the dramatic influence of increasing degradation rate constants,  $k_i$ , on alkenone concentrations and their downcore preservation. For example, when  $k_i$  is assumed to be  $1.0 \cdot 10^{-4} \text{ yr}^{-1}$ , then less than 1% of the originally deposited alkenones are preserved at a burial depth of 50 mbsf.

In general,  $\Delta$ SST increases with an increase in alkenone degradation rate constants,  $k_i$ , and preferential degradation factor,  $f_{C37:3}$ . An extremely high  $k_i$  ( $1.0 \cdot 10^{-3} \text{ year}^{-1}$ ) yields a large  $\Delta$ SST ( $\sim 27 \text{ °C}$ ) and extensive loss of C<sub>37</sub> alkenone ( $>> 99.9\%$ , results not shown). Yet, such an extreme distortion of the  $U_{37}^{K'}$  seems unlikely, given the fact that alkenones are generally well preserved, even in highly oxidising sediments [*e.g.*, *Prahl et al.*, 1989, 2003]. Lower  $k_i$  values ( $k_i < 2.5 \cdot 10^{-5} \text{ year}^{-1}$ ) result in lower alkenone degradation rates (fraction degraded at 250 mbsf is  $< 99\%$ ) and, thus, represent more plausible scenarios. In addition, Fig. 3-6 show that maximum  $\Delta$ SST is generally observed for mid-range  $U_{37}^{K'}(0)$ , and  $\Delta$ SST is smaller when initial  $U_{37}^{K'}(0)$  values are low or high (Fig. 3). This is especially true for high indices ( $U_{37}^{K'}(0) > 0.8$ ), which, of course, have a limited capacity to increase further. Even low initial  $U_{37}^{K'}(0)$

values are relatively robust under low degradation scenarios (Fig. 3). However, an increase in alkenone degradation, due to higher degradation rate constants (Fig. 5-6) and/or water and burial depths (a-b), shifts the  $\Delta$ SST maximum from mid  $U_{37}^{K'}(0)$  values towards lower  $U_{37}^{K'}(0)$  values ( $U_{37}^{K'}(0) < 0.2$ ) (Figure 6).

Similar to Scenario 1 (constant reactivity,  $k_i$ ), Scenario 2 simulations (RCM approach, decreasing reactivity with burial time/depth,  $k_i(z)$ ) can be assessed in the context of all parameters summarized in Table 1. Figures 7 and 8 illustrate changes in the  $U_{37}^{K'}$  derived SSTs and alkenone concentrations for each depositional environment and assuming  $a_i = 10^0$  yr and  $a_i = 10^3$  yr, respectively, and  $p_i = 10^{-1}$  (see above for figure details).

As already pointed out in section 2, a decrease in degradation rate constant  $k_i$  results in generally lower SST biases over the considered burial times. For higher initial alkenone reactivity ( $a_i = 10^0$  yr),  $\Delta$ SST does not exceed 6 °C (Figure 7), and  $\Delta$ SST < 2 °C for less reactive, but slowly decreasing alkenone reactivity ( $a_i = 10^3$  yr; Figure 8). Similar to Scenario 1, SST bias increases with an increase in preferential degradation factor ( $f_{C37:3}$ ), and the maximum  $\Delta$ SST is generally observed for the mid-range  $U_{37}^{K'}(0)$  values and decreases when  $U_{37}^{K'}(0)$  values are either low or high. Unlike Scenario 1 (constant reactivity), the most significant changes occur in the upper sediment layers and  $\Delta$ SST, as well as the degree of loss of alkenones (Figure 7-8, c-d) becomes attenuated with burial time/depth, due to the decrease in reactivity ( $k_i(z)$ ). Figure 9 illustrates the decrease in  $k_i(z)$  with burial time/depth, assuming  $p_i = 10^{-1}$  for  $a_i = 10^0$  yr (Figure 9a) and  $a_i = 10^3$  yr (Figure 9b). The lower  $a_i$  value results in a higher reactivity ( $k_i(0) \approx 10^{-1}$  yr<sup>-1</sup>) close to the sediment-water interface. However,  $k_i(z)$  decreases quickly in the upper sediment layers to  $k_i(z) < 10^{-5}$  yr<sup>-1</sup> at 50 mbsf and only decreases very slowly with increasing burial time/depth. The higher  $a_i$  value results in a lower reactivity ( $k_i(0) \approx 10^{-4}$  yr<sup>-1</sup>) close to the sediment-water interface, but decreases very slowly with burial time/depth. However, at greater burial depth, where burial time  $t \gg a_i$ , alkenone reactivity approaches

similar values as for lower  $a_i$  values ( $k_i(z) < 10^{-5} \text{ yr}^{-1}$ ) because Eq. 8 becomes dominated by burial time instead of  $a_i$ . Thus, even with distinct  $k_i(0)$ , increasing burial time/depth yields similar  $k_i(z)$ -values and these change much slowly than those of upper sediment layers. The rapid decrease in  $k_i(z)$  means that the degradation induced bias in SST is small and generally does not exceed the  $U_{37}^{K'}$  calibration error. In detail, high  $a_i$  values (Fig. 9b) reflect an overall low reactivity and yield a slow downcore decrease in  $k_i(z)$ , resulting in minor changes in SST (Fig. 8). The largest  $\Delta\text{SST}$  ( $\sim 6^\circ\text{C}$ ) are generally associated with low  $a_i$  value ( $a_i = 10^{-1} \text{ yr}$ ) and high preferential degradation factors  $f_{C_{37:3}} = 1.5$  (Fig. 7). Such low  $a_i$  values produce the most dramatic decrease in  $k_i(z)$  with depth (Fig. 9a) and, thus, represent the most heterogeneous distribution of alkenone reactivity.

Although unlikely, we can also explore the impact of differential evolution of alkenone reactivity with burial time, *i.e.* assuming different  $a_i$  values for the di- and tri-unsaturated alkenone pools ( $C_{37:3}$  more labile than  $C_{37:2}$ ). Figure 10 presents the simulated evolution of  $k_i(z)$  and SST with burial time/depth, assuming an initially high but rapidly decreasing reactivity for the  $C_{37:3}$  pool ( $a_{C_{37:3}} = 0.1 \text{ yr}$ ) and an initially low but slowly decreasing reactivity for the  $C_{37:2}$  pool ( $a_{C_{37:2}} = 100 \text{ yrs}$ ). This represents an extreme case scenario, since it assumes a large difference in the evolution of the reactivity with burial depth/time (Fig. 10a). The degradation rate constant  $k_{C_{37:3}}$  is three order of magnitude higher than  $k_{C_{37:2}}$  in the surface sediments. The rate constants then decrease at different rates with burial depth, before reaching similar magnitudes in deeper sediment layers ( $> 50 \text{ mbsf}$ ). Fig. 10b shows that the largest SST changes occur in the shallowest sediment layers, with the most pronounced  $\Delta\text{SST}$  ( $> 10^\circ\text{C}$ ) for  $U_{37}^{K'}(0) < 0.5$ . Deeper in the sediment, degradation rates and SST biases significantly slow down.

Overall, the decrease in  $k_i(z)$  with burial time/depth (Scenario 2) could explain the discrepancy between the fast degradation rates observed in laboratory experiments [Teece *et al.*, 1998; Rontani *et al.*, 2005, 2008], as well as field observations [Sun and Wakeham, 1994;

Gong and Hollander, 1999] and the long-term persistence of alkenones in the geological record [Brassell, 2014]. In addition, simulation results indicate that Scenario 2 (decrease in  $k_i(z)$  with burial time/depth) generally results in limited SST biases often below the detection limit. In contrast, Scenario 1 (constant  $k_i$ ) results in more pronounced SST bias and thus, serves as ‘worst case’ endmember scenario and provides a conservative framework to further investigate SST bias. The following sections assess the role of different controls on preferential alkenone degradation in altering  $U_{37}^{K'}$  during burial and thus, inducing biases in reconstructed SSTs.

## 4 Discussion

### 4.1 Disentangling the controls on SST bias during burial

Overall, both 1G (Scenario 1) and RCM (Scenario 2) simulations indicate that the following three factors control the magnitude of diagenetic modification on  $U_{37}^{K'}$  indices: 1) the extent of alkenone degradation, which, in turn, is controlled by the degradation rate constant,  $k_i$ , the burial depth,  $z$ , and the water depth; 2) the initial  $U_{37}^{K'}$  value,  $U_{37}^{K'}(0)$ ; and 3) the preferential degradation factor,  $f_{C37:3}$ . It is important to note that the influence of these three factors on  $\Delta$ SST is tightly linked. For instance, the extent of degradation exerts no impact on  $\Delta$ SST if there is no preferential degradation and vice versa. We also note that our simulations include scenarios in which intense alkenone degradation results in concentrations below the detection limit ( $< 5 \text{ ng g}^{-1}$ ), *i.e.* situations where  $U_{37}^{K'}$  could not be determined. Therefore, for the remainder of the discussion we only consider model results in which  $> 0.1\%$  of the original alkenone concentration is preserved.

#### 4.1.1 Extent of degradation

Scenarios 1 and 2 reveal that the extent of degradation – as a cumulative effect of  $k_i$ , as well as water and burial depths/time – is the major control on  $\Delta$ SST. The positive bias in  $U_{37}^{Kl}$  generally increases with an increasing extent of degradation during burial (Fig. 3-8).

The alkenone degradation rate constant,  $k_i$ , exerts an important control on the extent of degradation. The reconstructed  $\Delta$ SST increases from  $< 0.1$  °C to up to 27 °C with an increase in degradation rate from  $1.0 \cdot 10^{-5} \text{ yr}^{-1}$  to  $1.0 \cdot 10^{-4} \text{ yr}^{-1}$  (Fig. 3-6). This is particularly critical as alkenone degradation rate constants are difficult to constrain and also implicitly account for factors that control alkenone degradation during burial, but are not explicitly accounted for in the model [Arndt *et al.*, 2013]. Of all  $k_i$  values assessed in the present RTM study,  $k_i < 1.0 \cdot 10^{-5} \text{ yr}^{-1}$  seems to best represent the reactivity of alkenones in the sedimentary archive. This refers not only to SST biases ( $\Delta$ SST  $< 6.0$  °C), but also to the amounts of alkenones degraded. The adoption of faster, and constant,  $k_i$  (e.g.  $k_i > 5.0 \cdot 10^{-5} \text{ year}^{-1}$ ) results in an almost complete degradation of alkenones ( $>> 99.9\%$ ), which is inconsistent with their apparent persistence in the sedimentary record [Brassell, 2014]. However, experimentally derived  $k_i$  values obtained by Teece *et al.* [1998] for  $C_{37:3}$  are four orders of magnitude higher than what we infer to be our most realistic values, if those values are assumed to be constant with burial time/depth. Similarly, Rontani *et al.* [2005, 2008] also report  $k_i$  values in the order of  $10^{-1} \text{ yr}^{-1}$  for alkenones in degradation laboratory experiments. However, these rate constants were derived from fresh alkenone material in laboratory incubations, where conditions were optimized to investigate alkenone degradation. This experimental setting could result in a ‘priming effect’ and enhance the degradation of more recalcitrant material [Aller, 1994; Aller and Blair, 2006]. Therefore, they do not account for the complexity of natural conditions [Schouten *et al.*, 2010], and it seems likely that these experiments represent unrealistically high degradation rates compared to natural settings. Environmental conditions that likely account for the lower degradation rates

include changes in terminal electrons availability (TEA) (*e.g.* O<sub>2</sub> availability) and/or packing in macromolecular complexes or mineral particles, which would slow down or prevent microbial attack [see *Arndt et al.*, 2013 and references therein for overview].

The extent of alkenone degradation in sediments also depends on water and burial depths/times and thus, the physical depositional environment, which exerts a positive, albeit secondary control. Alkenones deposited in deeper waters experience a greater degree of degradation at similar burial depths, due to slower burial rates or in other words longer burial times [*Middelburg et al.*, 1997]. This effect is consistent with observational data. *Conte et al.* [1992] observed a rapid and significant (by 1-2 orders of magnitude) degradation of alkenones in deep North Pacific waters. In particular, burial depth and, thus, burial time controls the extent of degradation. Longer burial time (*i.e.* deeper depths in the sediment) allows for a longer exposure of alkenones to heterotrophic degradation, therefore resulting in more intensive degradation and ultimately a stronger bias in SST. This becomes evident in Fig 3-6 (Scenario 1). Assuming the least dramatic condition (Fig. 3), the maximum perturbation in SST increases from < 2 °C at 50 mbsf to up to 6 °C at 250 mbsf. Alternatively, scenarios with higher  $k_i$  values (Fig. 6), yield  $\Delta$ SST of 10 °C at 50 mbsf and 27 °C at 250 m. Although unrealistic, the latter illustrates how burial depth, as a component of extent of degradation, controls SST biases. However, in Scenario 2, burial time/depth becomes less important with time/depth (Fig. 7-8), due to the decrease of  $k_i(z)$  (Fig. 9). In fact, under such conditions,  $k_i(z)$  and SST bias become attenuated at greater depths.

#### 4.1.2 The initial $U_{37}^{K'}$ value

Initial  $U_{37}^{K'}$  values at the SWI ( $U_{37}^{K'}(0)$ ) exert a non-linear effect on  $\Delta$ SST during burial and mid-range values ( $U_{37}^{K'} \approx 0.5$ ) generally exhibit the most pronounced SST bias (Fig. 3-4 and 7-8). As *Hoefs et al.* [1998] previously pointed out, such a result is mathematically expected and is



the likely explanation for the disagreement between experimental alkenone degradation studies. Under similar conditions, *Rontani et al.* [1997] and *Teece et al.* [1998] found no significant degradation-induced changes in  $U_{37}^{K'}$ , whereas *Rontani et al.* [2005] later observed a positive degradation-induced bias of 0.1  $U_{37}^{K'}$  units. *Rontani et al.* [2005] argued that the different outcome of these degradation experiments can be explained by different initial  $U_{37}^{K'}$  values: 0.49 in *Rontani et al.* [2005]; 0.75 in *Teece et al.* [1998]; and 0.85 in *Rontani et al.* [1997]. Model results confirm that  $U_{37}^{K'}$  values are relatively robust towards preferential degradation for both high and low  $U_{37}^{K'}(0)$  when the extent of degradation is low (low  $k_i$ , shallow sediment depth/short burial times; Fig. 3-4 and 7-8). However, low  $U_{37}^{K'}(0)$  initial conditions become more sensitive to diagenetic alteration under intense degradation scenarios (high  $k_i$ , low sedimentation rate, deep burial depth/ long burial times), and maximum  $\Delta$ SST shifts to low  $U_{37}^{K'}(0)$  under such conditions (Fig 5-6).

The combined effects of degradation extent and  $U_{37}^{K'}(0)$  are illustrated in Fig. 11. This shows how the extent of degradation exerts a first order control on  $\Delta$ SST, with  $U_{37}^{K'}(0)$  exerting a lesser and non-linear SST bias. Moreover,  $U_{37}^{K'}(0) = 0.5$  is most prone to SST biases when degradation is low and lower values of  $U_{37}^{K'}(0)$  are more prone to SST biases when degradation is extensive.

#### 4.1.3 Preferential degradation factor

The preferential degradation factor  $f_{C37:3}$  is the parameter that ultimately controls the difference between the degradation rates of the di- and tri-unsaturated  $C_{37}$  alkenones. Regardless of the environmental triggers for  $C_{37}$  selective degradation (see Introduction), RTM results show that an increase in  $f_{C37:3}$  and thus, a more pronounced preferential degradation of  $C_{37:3}$  generally leads to a pronounced increase in  $\Delta$ SST (Figure 3-8). However, the sensitivity of  $U_{37}^{K'}$  and  $\Delta$ SST

to an increase in  $f_{C37:3}$  depends on the extent of degradation and thus, the degradation rate constant  $k_i$ . Even high  $f_{C37:3}$  values of 1.5 only induce small  $\Delta$ SSTs unless the degradation rate constant is large.

Additionally, the impact of  $f_{C37:3}$  on  $\Delta$ SST is also dependent on the  $U_{37}^{K'}(0)$ . As previously pointed out,  $\Delta$ SST is mostly affected when  $U_{37}^{K'}(0) = 0.5$  and the extent of degradation is low. Thus, the preferential degradation factor  $f_{C37:3}$  most impacts mid-range values of  $U_{37}^{K'}(0)$ . Figure 12, assuming a constant degradation rate (*e.g.*  $k_i = 5 \cdot 10^{-5} \text{ yr}^{-1}$ ), allows us to explore the effects of  $f_{C37:3}$  and  $U_{37}^{K'}(0)$  on  $\Delta$ SST. For the lowest  $f_{C37:3} = 1.1$  (Fig. 12a), the change in SST shows a linear downcore trend; the  $U_{37}^{K'}(0) = 0.5$  yields the largest SST perturbation, whereas the high-end  $U_{37}^{K'}(0)$  value is the least altered. Increasing the preferential degradation factor to  $f_{C37:3} = 1.2$  (Fig. 12b) and  $f_{C37:3} = 1.3$  (Fig. 12c) results in a non-linear  $\Delta$ SST, as well as a shift towards maximum  $\Delta$ SST occurring at lower  $U_{37}^{K'}(0)$  values. These results arise because increasing  $f_{C37:3}$  values results in preferential loss of  $C_{37:3}$  alkenone and therefore, stronger biases at the lower-end of  $U_{37}^{K'}(0)$ . Overall and as expected, it is clear that  $f_{C37:3}$  exerts a direct control on SST biases. However, only high  $f_{C37:3}$  values in combination with intense degradation rates (*i.e.* high  $k_i$ ) induce  $\Delta$ SST larger than the  $U_{37}^{K'}$  calibration error. Model results emphasize the need to better constrain  $f_{C37:3}$  values in natural settings and to identify the factors that control the preferential degradation of  $C_{37:3}$ . Laboratory incubation experiments performed by Teece *et al.* [1998] found negligible differences in  $C_{37:2}$  and  $C_{37:3}$  alkenone degradation rates, yielding  $f_{C37:3} \approx 1.0$ . Later experiments conducted by Rontani *et al.* [2008] were able to produce up to 3 °C positive SST biases; given that  $U_{37}^{K'}(0) > 0.7$  in that study, a 3 °C  $\Delta$ SST yields  $f_{C37:3} \sim 1.2$ . Similar analyses can be conducted for field studies (Table 3) and explain apparently contradictory behavior. For example, at the Peruvian Margin, McCaffrey *et al.* [1990] found an alkenone loss of 30% in the top 1 cm of sediments underlying

anoxic waters, but  $U_{37}^{K'}$  was largely unaffected. Our model results show that when  $f_{C37:3} < 1.5$ , the extent of degradation must exceed 50% to yield measurable  $\Delta SST$ . *Prahl et al.* [1989, 2003] observed extensive loss of alkenones in the Madeira Abyssal Plain (MAP) turbidites (86 – 99%), but only minor changes in  $U_{37}^{K'}$  indices ( $\Delta SST < 1.3$  °C for  $U_{37}^{K'}(0) \geq 0.7$ ). Model results indicate that this requires a preferential degradation factor  $f_{C37:3}$  between 1.1 and 1.2 for the MAP turbidites. *Hoefs et al.* [1998] reported a > 99% extent of degradation associated with a +0.17 increase in  $U_{37}^{K'}$  indices (*i.e.*  $\Delta SST \sim 5$ °C), which yields an  $f_{C37:3} \sim 1.3$  in our simulations. There is also evidence that  $f_{C37:3}$  differs between oxic and anoxic settings. In the Santa Monica Basin sediments, *Gong and Hollander* [1999] compared  $U_{37}^{K'}$  records from two adjacent areas and observed a difference in reconstructed SST of up to 4 °C, with oxic settings recording higher temperatures than anoxic ones. However, the extent of degradation was 60% for both settings, indicating that  $f_{C37:3}$  differed between the two, being  $\sim 1.3$  and  $\sim 1.0$  in the oxic and anoxic settings (assuming no preferential degradation at the anoxic setting), respectively.

Preferential degradation under aerobic conditions [*Hoefs et al.*, 1998; *Gong and Hollander*, 1999] has been attributed to preferential degradation of the tri-unsaturated  $C_{37:3}$  alkenone via double bond epoxidation [*Rontani et al.*, 2008]. This process occurs more effectively at position  $\omega 29$ , only present on the  $C_{37:3}$  alkenone, rather than positions  $\omega 15$  and  $\omega 22$  which occur on both  $C_{37}$  alkenones, and is suggested to be mediated by the bacterial strain *Dietzia maris* sp. S1 [*Rontani and Wakeham*, 2008; *Zabeti et al.*, 2010]. Despite this, it appears that aerobic microbially-mediated selective degradation occurs in a non-systematic way [*Rontani et al.*, 2005, 2008; *Rontani and Wakeham*, 2008], which compromises our ability to quantify and predict its controls on preferential degradation in marine sediments. Moreover, as discussed above,  $f_{C37:3}$  appears to be consistently greater than 1 in a variety of settings such that it cannot be solely dependent on oxic/anoxic conditions [*Rontani and Wakeham*, 2008].

## 4.2 Implications for $U_{37}^{K'}$ paleothermometry

Our model exploration of alkenone degradation provides a quantitative framework for assessing SST reconstructions. Here, we illustrate how model results can be used to explore or offer alternative explanations for SST mismatches in the sedimentary archive.

First, the magnitude of SST bias will depend on the initial  $U_{37}^{K'}$  value. As previously discussed (Section 4.1.2), high  $U_{37}^{K'}$  values are least affected, implying that the alkenone-derived SST records from relatively warm settings will have been less affected than those from colder settings [e.g., *Rodrigo-Gámiz et al.*, 2016].

Second, the extent of degradation exerts a very strong control on SST reconstructions. The *Müller et al.* [1998] SST calibration is characterized by a standard error of  $\pm 1.5$  °C, and preferential  $C_{37:3}$  degradation that produces biases  $> 1.5$  °C are thus of particular concern. Although previous studies argued that  $\Delta SST > 1.5$  °C warm biases do occur [*Madureira et al.*, 1995; *Hoefs et al.*, 1998; *Gong and Hollander*, 1999; *Pagani et al.*, 1999], model results show that if the extent of alkenone degradation is low ( $< 50\%$ ), such biases require a high preferential degradation factor, i.e.  $f_{C37:3} \geq 1.5$  (Figure 11). This scenario seems unrealistic since it assumes a  $C_{37:3}$  degradation rate that is at least 50% faster than  $C_{37:2}$ . It is also inconsistent with most experimental and field investigations (see above). Yet, if the extent of degradation is high (50 to 99.9%), SST biases  $> 1.5$  °C are simulated for  $f_{C37:3}$  values ranging from 1.1 to 1.4. In the most extreme degradation scenario ( $> 99.9\%$ ), any  $f_{C37:3} > 1.0$  can produce SST biases above 1.5 °C (Fig. 11). However, as already pointed out, such high degradation rates significantly reduce alkenone concentrations, rendering the analytical determination of  $U_{37}^{K'}$  ratios challenging. In fact, SST biases can also arise from instrumental errors when concentrations are extremely low [*Grimalt et al.*, 2000, 2001].

Overall and holding other factors equal, reconstructed SSTs are most biased in older sediments, where the extent of degradation will be most severe for a given depositional setting.

Although this is valid for both scenarios, in Scenario 2 (decrease in  $k_i(z)$  with burial time/depth), degradation rapidly slows down in very old/deeply buried sediments and differences in SST bias thus become negligible when comparing sediment layers/burial times  $t \gg a_i$ . Model results reveal how several mathematical factors mitigate and exacerbate that effect. Assuming steady state, degradation is most rapid in shallow sediments and slows with depth, an effect exacerbated in Scenario 2. In contrast, the impact of degradation on  $U_{37}^{K'}$  increases as degradation approaches its mathematical limit (*i.e.* 100%). These two factors work in tandem. Therefore, we would expect  $\Delta$ SST biases to occur throughout the burial time and from the entire sediment column rather than solely in deep sediments. Therefore, it is useful to evaluate  $U_{37}^{K'}$ -derived SST records against those based on other proxies in both recent and older sediment records.

#### 4.2.1 Assessing potential degradation bias in recent sedimentary records

In general, alkenone-derived SST estimates agree well with other SST reconstructions for shallow geological time periods ( $< 500$  kyrs), indicating that diagenetic alterations of the  $U_{37}^{K'}$  paleothermometer are negligible. For example,  $U_{37}^{K'}$  and Mg/Ca (*Globigerinoides sacculifer*) SSTs estimates from the Western Equatorial Pacific (WEP) are of a similar magnitude over the past 30 kyr [*de Garidel-Thoron et al.*, 2007]. This was observed despite relatively low alkenone concentrations and possibly extensive degradation, suggesting that preferential degradation had only a minor impact (*i.e.*  $f_{C37:3} \approx 1.0$ ). The glycerol dialkyl glycerol tetraether (GDGT)-based TEX<sub>86</sub> (tetraether index of tetraethers consisting of 86 carbons) proxy [*Schouten et al.*, 2002] is a widely used organic paleothermometer [*e.g.*, *Schouten et al.*, 2013] which also exhibits a close agreement with  $U_{37}^{K'}$ -derived SSTs over shallow timescales. For example,  $U_{37}^{K'}$  and TEX<sub>86</sub> SST estimates obtained from core tops within the Arabian Sea (NIOP905 and 74KL) match modern mean annual SST values for that area [*Huguet et al.*, 2006]. In the Eastern

Mediterranean (GeoB7702-3),  $U_{37}^{K'}$  and TEX<sub>86</sub> also record similar trends and absolute SST values over the past 27 kyr [Castañeda *et al.*, 2010].  $U_{37}^{K'}$  and TEX<sub>86</sub>-based reconstructions agreed well even in depth intervals where alkenone concentrations were low, indicating that even a high extent of degradation did not alter the  $U_{37}^{K'}$  signal at these sites. In the Western Mediterranean, Huguet *et al.* [2011] reported similar temperature trends between  $U_{37}^{K'}$  and TEX<sub>86</sub> for the last 244 – 130 kyrs. Although, TEX<sub>86</sub> absolute SST were higher than  $U_{37}^{K'}$  SST, the difference rarely exceeded  $< 3$  °C, which is within both proxy calibration errors (and inconsistent with the latter being biased to warm temperatures). In fact, in many cases where TEX<sub>86</sub> and  $U_{37}^{K'}$  -derived SSTs differ, it is due to the latter being colder rather than warmer [Huguet *et al.*, 2006; Castañeda *et al.*, 2010; Grauel *et al.*, 2013]; and in the few settings where the opposite is observed [Lopes dos Santos *et al.*, 2010; McClymont *et al.*, 2012; Seki *et al.*, 2012; Li *et al.*, 2013], it is often attributed to the depth of GDGT production.

#### 4.2.2 Assessing potential degradation bias in older sedimentary records

In general, inferred degradation biases have been largely limited to deep time (Miocene and older) settings. For instance, the absence of tri-unsaturated alkenone in many Miocene sediments from DSDP (Deep Sea Drilling Program) sites 588, 608 and 730 results in  $U_{37}^{K'}$  values of 1 and therefore, SST  $> 28$  °C [Pagani *et al.*, 1999]. RTM results suggest that these observations might indicate long-term preferential consumption of C<sub>37:3</sub> – and indeed alkenone concentrations are low in these sediments. However, such a scenario would require extensive degradation and, although mathematically possible, remains inconsistent with the lack of such extensive degradation in younger settings. Therefore, we suggest, based on insights gained through the model investigation, that at the DSDP sites 588, 608 and 730 Miocene SST records have not been extensively affected by selective degradation and that SSTs were indeed relatively high. It is worth noting that one rationale for those suggestions was the much higher

temperatures recorded by alkenones than by planktonic foraminifera  $\delta^{18}\text{O}$ . However, those isotopic records have almost certainly been biased by diagenetic recrystallization [e.g., *Pearson et al.*, 2001, 2007], and these records have now been discarded [*Pagani et al.*, 2010]. This illustrates some of the challenges associated with multi-proxy SST reconstructions and the pitfalls of interpreting proxies with preconceived notions of relative fidelity.

In Paleogene sediments, more complex temperature relationships have been observed, with offsets between  $U_{37}^{K'}$  and foraminiferal  $\delta^{18}\text{O}$ -derived SSTs ranging from 0 to 10 °C [*Pagani et al.*, 2005; *Liu et al.*, 2009]. Again, this could be due to a long-term selective degradation of alkenones or diagenetic alteration of foraminifera  $\delta^{18}\text{O}$  values [*Pearson et al.*, 2001, 2007; *Pagani et al.*, 2010]. Our RTM results support the latter, because such significant SST bias at such high  $U_{37}^{K'}$  indices is difficult to achieve without nearly complete degradative loss of the alkenones.

Nonetheless, we do acknowledge that in some settings large SST off-sets between alkenones and other proxies are observed and more difficult to explain. For example, *Weller and Stein* [2008] observed that  $U_{37}^{K'}$ -derived SSTs in the Eocene Arctic Ocean were up to 10 °C higher than the  $\text{TEX}_{86}$ -derived SSTs reported by *Brinkhuis et al.* [2006]. A recent re-analysis of  $\text{TEX}_{86}^{\text{H}}$ -derived temperatures suggests that the offset between  $\text{TEX}_{86}^{\text{H}}$  and  $U_{37}^{K'}$  in deep-time settings could result from a calibration bias [*Ho and Laepple*, 2016]; however, if this assumption is valid that would yield higher  $\text{TEX}_{86}^{\text{H}}$  SSTs. *Weller and Stein* [2008] argued that the observed offset arises from the distinct ecological characteristics of alkenone and GDGT producers, as they likely occupy different habitats in the water column. This seems likely because model results, although showing that preferential degradation of  $\text{C}_{37:3}$  can yield 10 °C offsets, show that this can only happen under extreme degradation conditions.

The RTM approach applied here illustrates how such interpretations can be tested in more than simply an *ad hoc* manner when reconstructed SSTs are perceived to be too high,

particularly when looking at absolute SST values, since SST differences (relative values) are expected to be less biased. In particular, reconstructed SSTs should be interpreted in the context of the most important factors that could potentially drive putative SST biases: the presumed initial  $U_{37}^{K'}(0)$  value and the extent of alkenone degradation. RTM results allow exploring the robustness of relative temperature changes resulting from contrasting  $U_{37}^{K'}(0)$  by shifting temperature changes (higher SST shifted minimally, whereas lower SST shifted more strongly).

#### 4. Conclusions

RTM simulations show that preferential degradation of tri- over di-unsaturated C<sub>37</sub> alkenone can potentially alter the original signal of the  $U_{37}^{K'}$  paleothermometry and consequently produce positively biased SST records. Results from a plethora of environmental and degradation scenarios indicate that a combination of factors can result in a large range of possible SST biases, but the greatest changes require extensive alkenone degradation. Positively biased SST records are also governed by the differential degradation factor between C<sub>37</sub> alkenones ( $f_{C37:3}$ ), which based on various modern studies appears to vary between 1 and 1.5; however, these extreme values seem limited to only some settings. Initial  $U_{37}^{K'}(0)$  plays a secondary role on the SST changes. Not all of the simulated scenarios are realistic; those that yield maximum SST biases would require that alkenones be effectively removed from the sedimentary record – a direct consequence of the major control exerted by the degree of degradation. However, modest SST biases are associated with realistic assumptions about degradation rates, consistent with environmental studies (*i.e.* in oxidised turbidites). Consequently, we caution against the interpretation of  $U_{37}^{K'}$  indices when alkenone concentrations are low, especially if low concentrations are a direct result of extensive degradation.



RTM results offer a possible complementary explanation for SST off-sets between  $U_{37}^{K'}$  and other paleotemperature proxies found in the geological record and help elucidate mismatches between proxies. Additionally, it can be useful to avoid erroneous paleoreconstructions and interpretations derived from  $U_{37}^{K'}$  diagenetically altered signals. Nevertheless, comparisons between our RTM results and the alkenone sedimentary record suggest that, in general,  $U_{37}^{K'}$ -SST records have not been as extensively altered as sometimes assumed.

## Tables and figure captions

**Table 1:** Selective degradation alkenones RTM components

Parameter	Description	Value/Range	Unit
C	$C_{37:2}$ or $C_{37:3}$ concentration at depth		$\mu\text{g cm}^{-3}$
$C_0$	$C_{37:2}$ or $C_{37:3}$ concentration at SWI	0.5 – 4.5	$\mu\text{g g}^{-1}$
$k_i$	Degradation rate constant	$10^{-5} - 10^{-3}$	$\text{year}^{-1}$
$a_i$	Apparent initial age	$10^{-1} - 10^4$	year
$p_i$	Shape parameter of alkenones distribution	$10^{-2} - 10^0$	
$D_{\text{bio}}$	Diffusion bioturbation coefficient	12.05; 25.06	$\text{cm}^2 \text{ year}^{-1}$
$\omega$	Burial velocity	0.16; 0.36	$\text{cm year}^{-1}$
$\rho$	Sediment density	2.5	$\text{g cm}^{-3}$
$z$	Sediment depth	0 – 25.000	cm
$z_{\text{bio}}$	Bioturbation depth	10	cm
	Water depth	200; 1.000	m
$U_{37}^{K'}(0)$	$U_{37}^{K'}$ initial fractionation at SWI	0.1 – 0.9	
$f_{C37:3}$	$C_{37:3}$ preferential degradation factor	1.1 – 1.5	
SST	Sea surface temperature*	$U_{37}^{K'} = 0.033 \cdot \text{SST} + 0.044$	$^{\circ}\text{C}$
$\Delta\text{SST}$	SST excursion or bias from SWI to depth	$\text{SST}_{\text{SWI}} - \text{SST}_{\text{Depth}}$	$^{\circ}\text{C}$

\*Müller et al. [1998];

**Table 2.** Sea surface temperature biases and total alkenone preservation in sediments from 50 and 250 mbsf, based on different 1G RTM scenarios

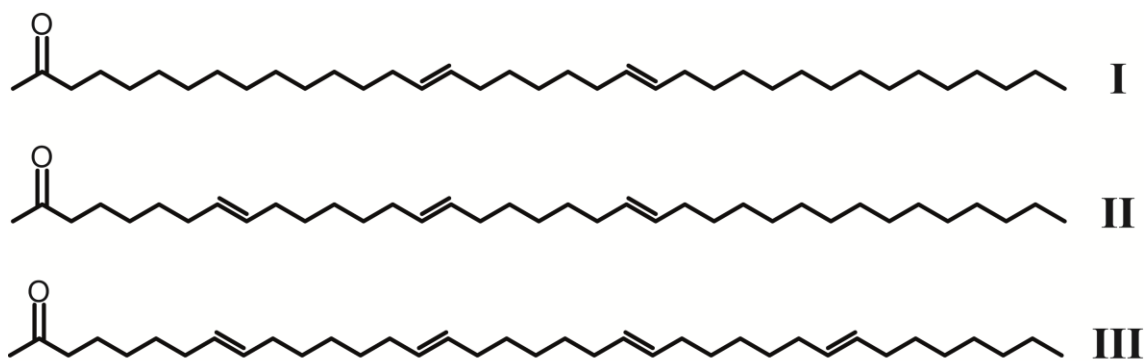
$k_i$ (year <sup>-1</sup> )	Minimum $\Delta$ SST (°C) <sup>a</sup>		Maximum $\Delta$ SST (°C) <sup>b</sup>		Fraction of alkenone preserved (%) <sup>b</sup>	
	200 <sup>c</sup>	1000 <sup>c</sup>	200 <sup>c</sup>	1000 <sup>c</sup>	200 <sup>c</sup>	1000 <sup>c</sup>
$1.0 \cdot 10^{-5}$	0.03	0.08	2.6	5.7	48.1	20.1
$2.5 \cdot 10^{-5}$	0.09	0.20	6.4	13.5	16.6	1.9
$5.0 \cdot 10^{-5}$	0.18	0.39	12.3	22.4	2.8	0.4
$1.0 \cdot 10^{-4}$	0.35	0.74	20.8	27.1	< 0.1	< 0.1
$1.0 \cdot 10^{-3}$	2.21	2.8	27.2	27.2	<<0.1	<<0.1

<sup>a</sup>at 50 mbsf; <sup>b</sup>at 250 mbsf; <sup>c</sup>water depth;

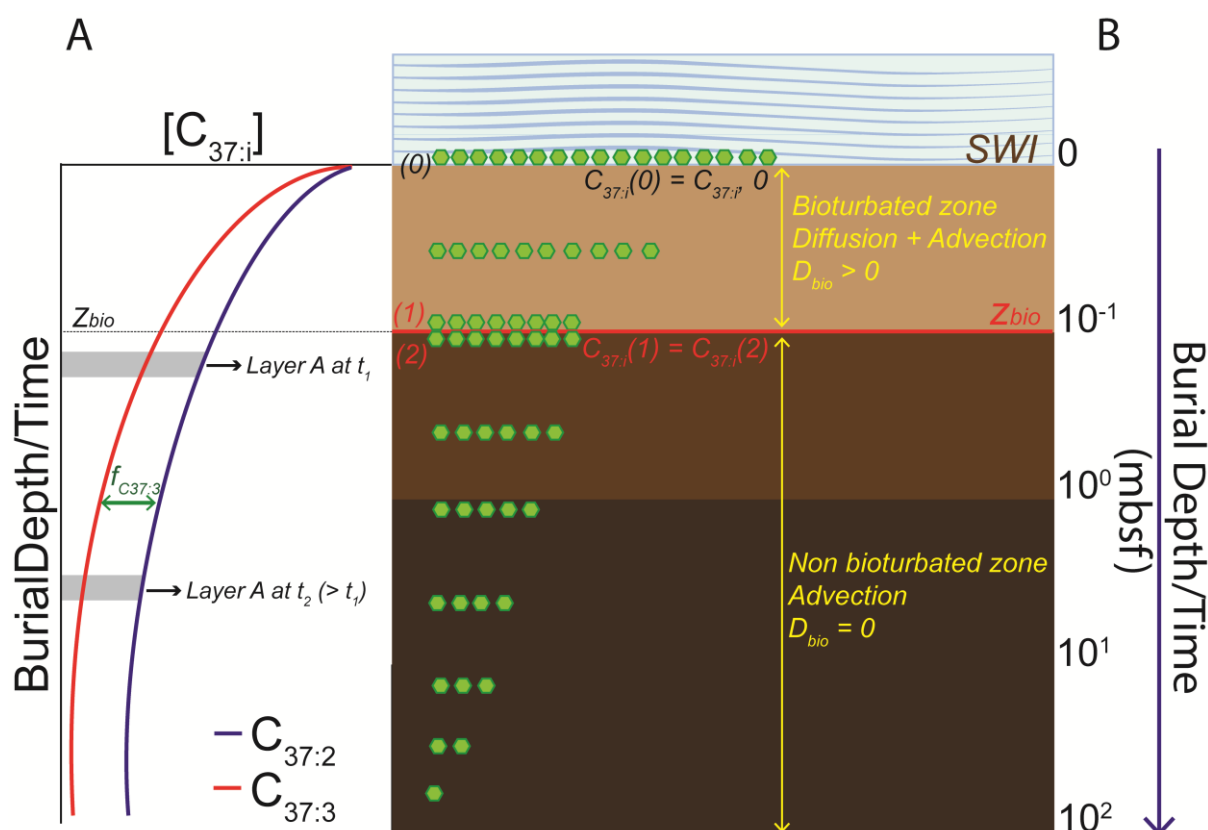
**Table 3.** Published experimental and field derived alkenones degradation data summarizing the main preferential degradation parameters

Study	Setting	$U_{37}^{K'}(0)$	$\Delta SST$	Extent of degradation
Teece et al., 1998	Experimental <sup>1</sup>	0.74	< 1.0	85
	Experimental <sup>2</sup>	0.59	<0.1	40
Rontani et al., 2005	Experimental <sup>1</sup>	0.49	~ 3.0	93
	Experimental <sup>3</sup>	0.49	<0.1	95
Rontani et al., 2008	Experimental <sup>1</sup>	0.77	~ 3.0	78
McCaffrey et al., 1990	Peruvian Margin	0.7	< 0.5	30
Prahl et al., 2003	MAP - 140 ky	0.71	<0.5	86
	MAP - Late Pliocene	0.91	<0.5	95
	MAP - Early Pliocene	0.91	<0.5	98
	MAP - Late Miocene	0.94	<0.5	99
Hoefs et al., 1998	MAP - Late Pliocene	0.77	0.5	>99
	MAP - Early Pliocene	0.86	2.0	>99
	MAP - Late Miocene	0.87	0.6	>99
	MAP - Middle-late Miocene	0.92	2.5	>99
Gong and Hollander, 1999	Santa Monica Basin <sup>4</sup>	0.54	2.5 - 4	60

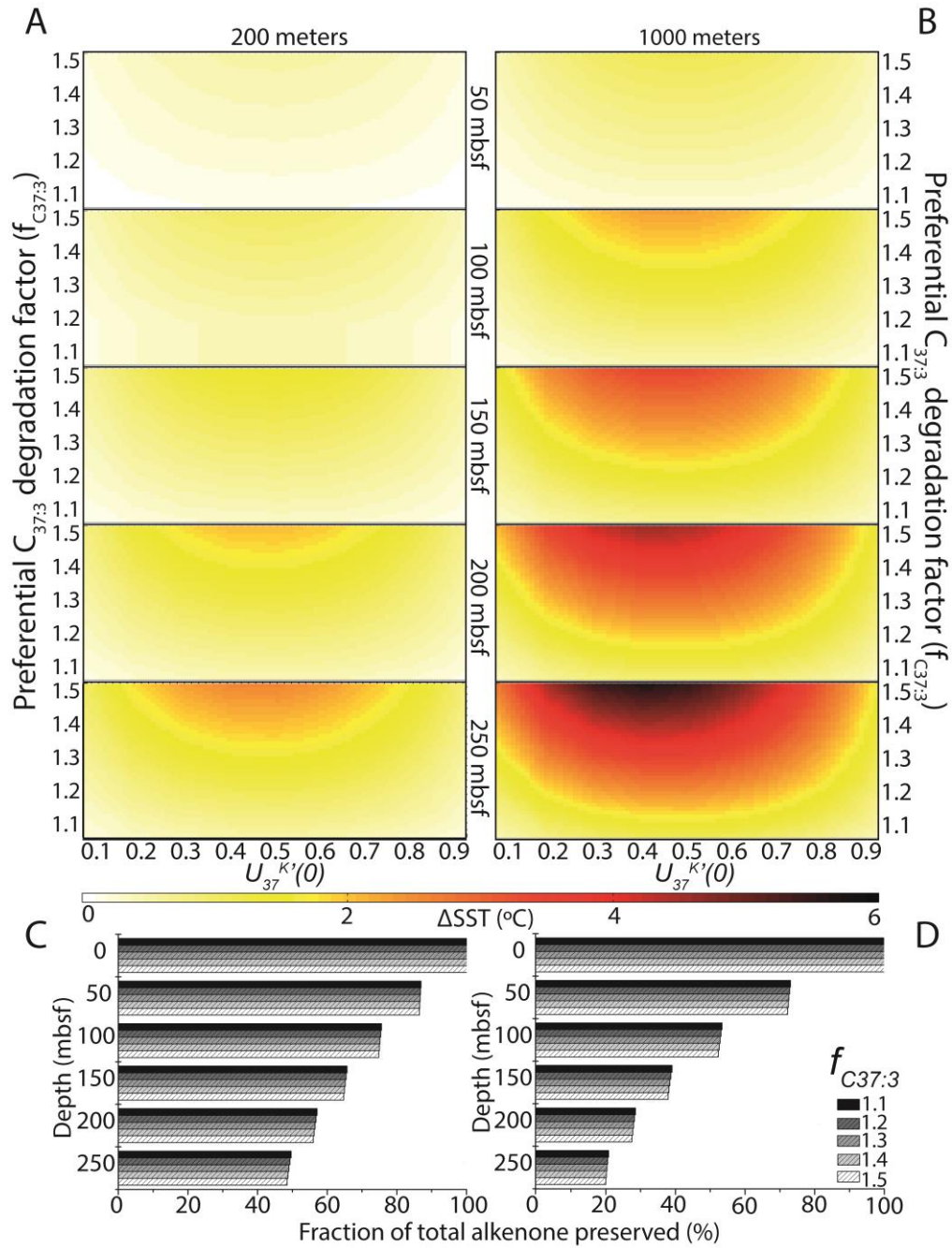
<sup>1</sup>Oxic; <sup>2</sup>Sulphate reduction; <sup>3</sup>Denitrification; <sup>4</sup>Oxic/Anoxic; MAP – Madeira Abyssal Plain;



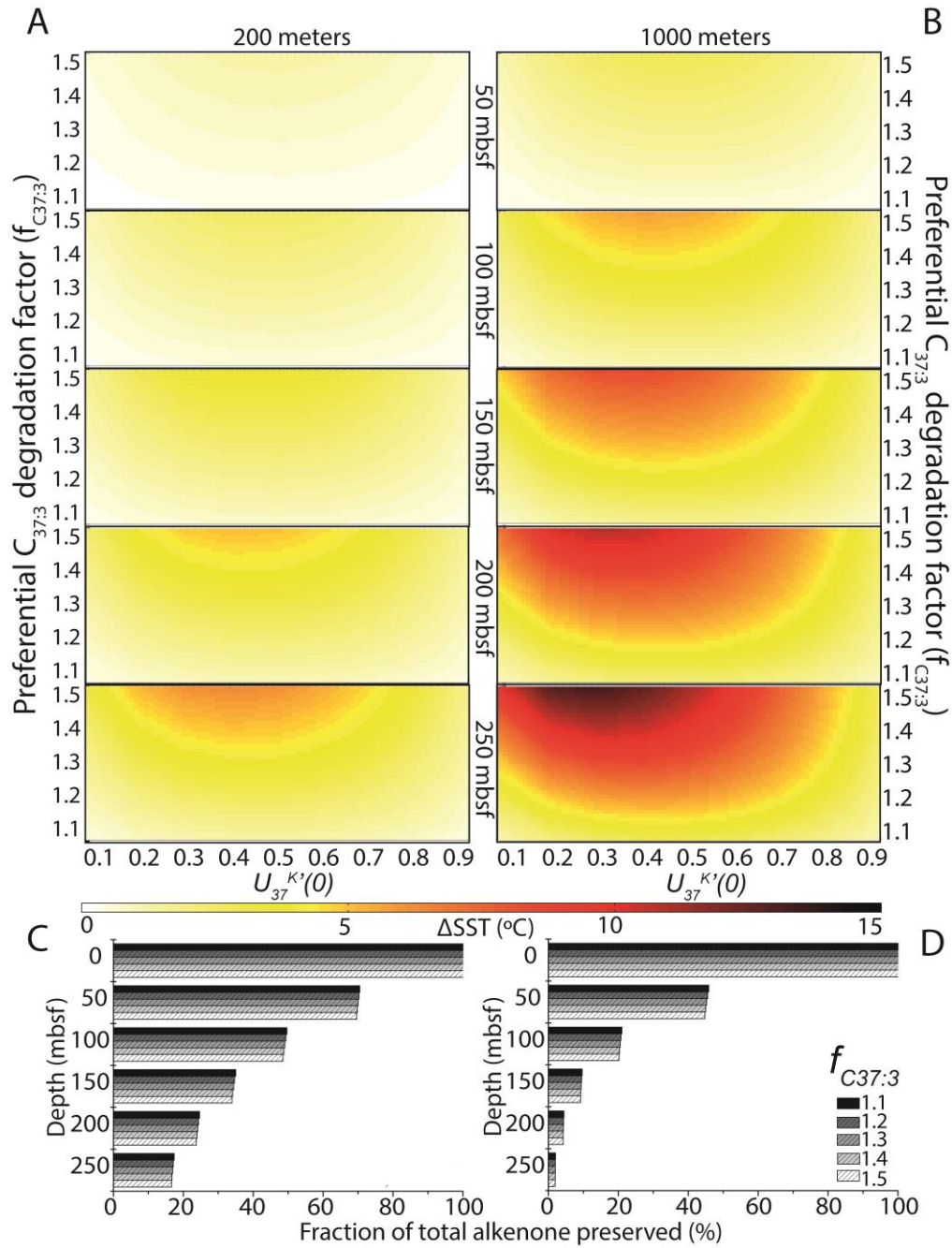
**Figure 1.** Chemical structure of C<sub>37</sub> alkenones. (I) Heptatriaconta-8,15-dien-2-one – C<sub>37:2</sub>; (II) Heptatriaconta-8,15,22-trien-2-one – C<sub>37:3</sub>; (III) Heptatriaconta-8,15,22,29-tetraen-2-one – C<sub>37:4</sub>.



**Figure 2.** Schematic representation of one-dimensional alkenone degradation in marine sediments with main model elements. (a) Hypothetical downcore evolution of  $C_{37}$  alkenone concentrations ( $C_{37:i}$ ) as a result of transport and reaction processes during burial in the sediment; the blue line represents  $C_{37:2}$  alkenone concentrations, whereas the red line represents  $C_{37:3}$  concentrations. The green arrow indicates the preferential degradation factor,  $f_{C_{37:3}}$ , of  $C_{37:3}$  over  $C_{37:2}$  during selective degradation. (b) Conceptual representation of  $C_{37}$  alkenone burial and degradation as a modelled sediment column; the green hexagons represent  $C_{37}$  alkenone concentrations and the red line marks the limit of bioturbated zone ( $Z_{bio}$ ).  $D_{bio}$  denotes the bioturbation diffusion coefficient. SWI represents the sediment water interface.

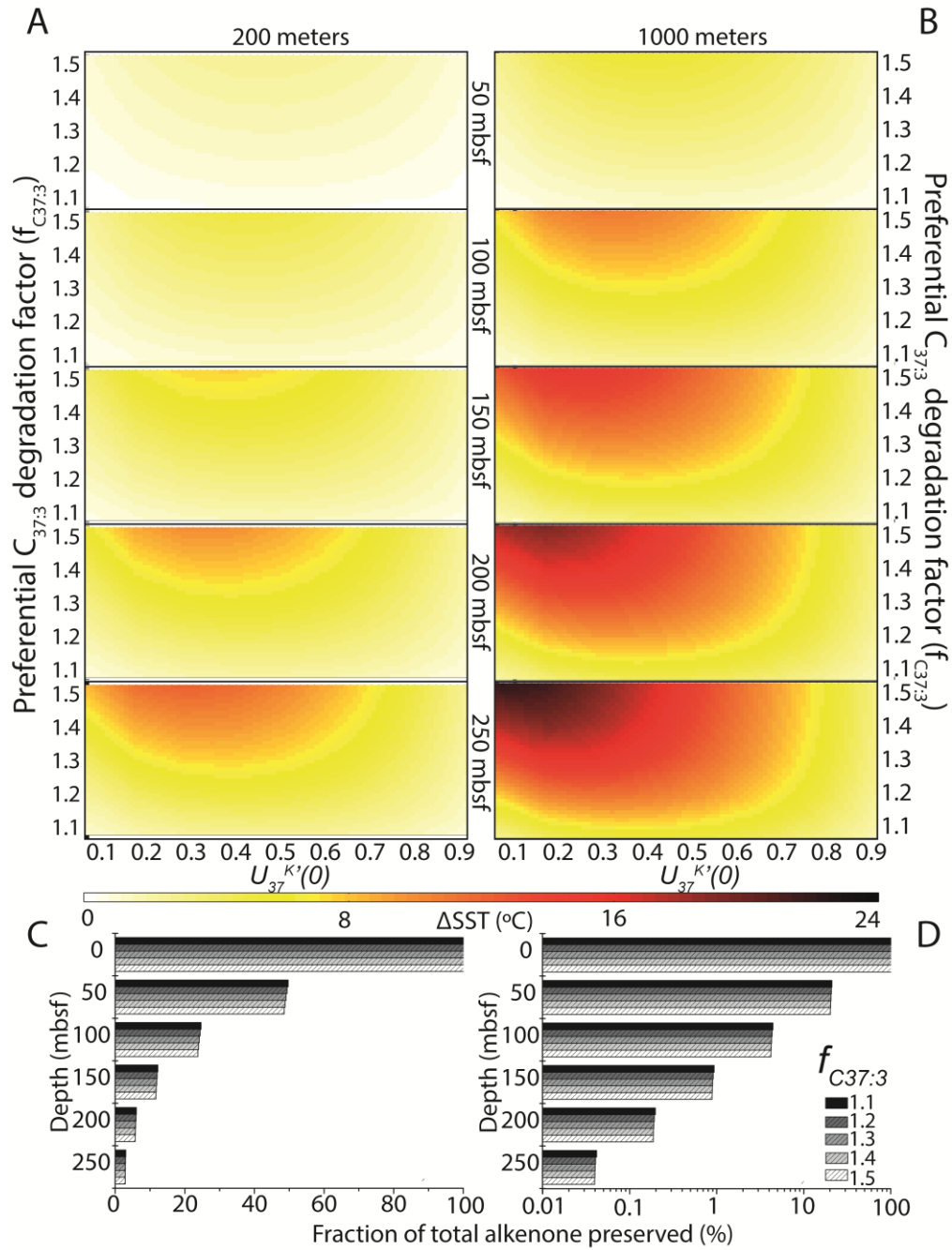


**Figure 3.** Interpolated SST positive bias and total alkenones preserved in sediment resulting from selective degradation of alkenones in a 1G-RTM simulation assuming a rate constant ( $k_i$ ) of  $1.0 \cdot 10^{-5} \text{ year}^{-1}$ . (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth.  $\Delta SST$  denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}(0)$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C_{37:3}}$  denotes differential degradation factor between  $C_{37:3}$  and  $C_{37:2}$  alkenones.

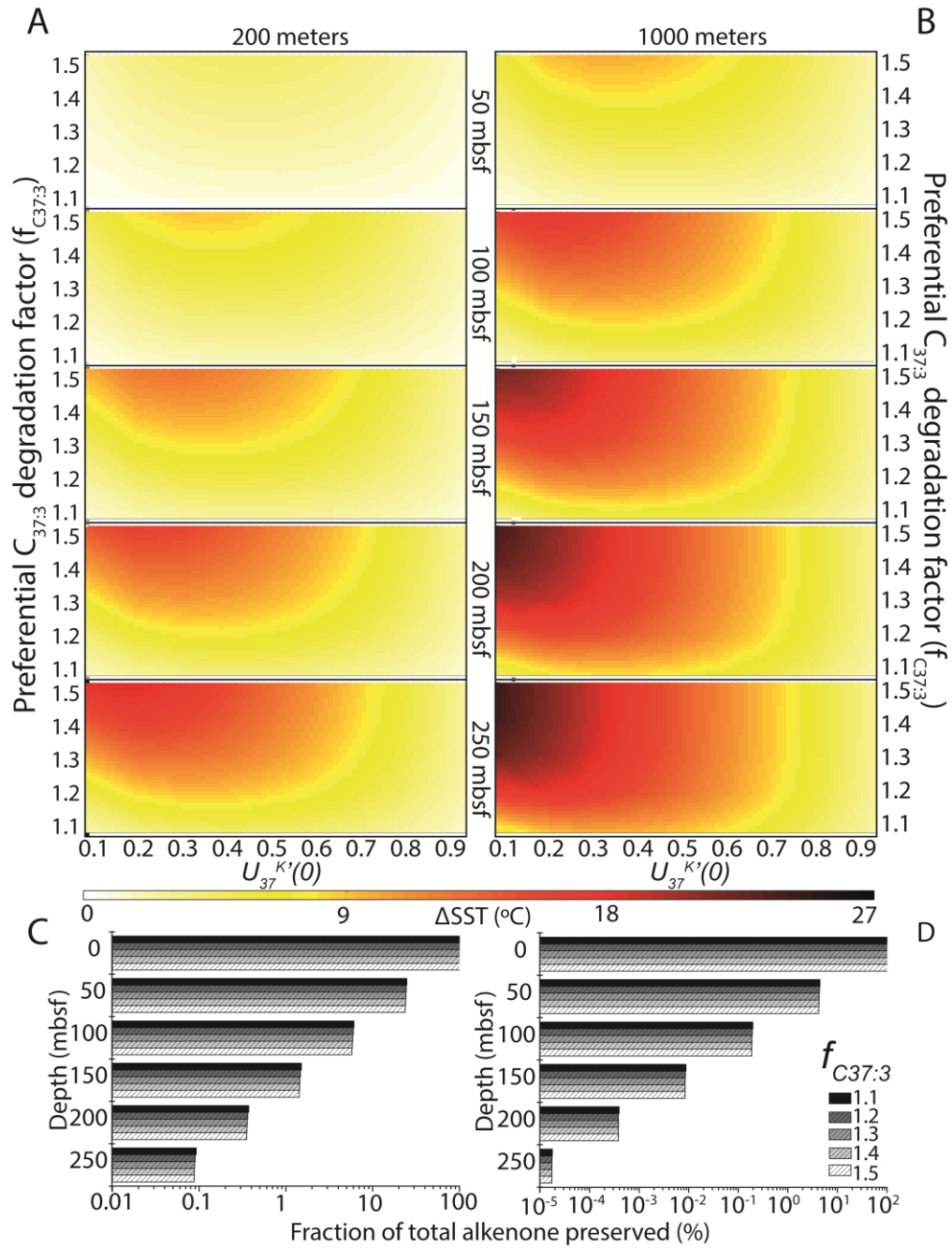


**Figure 4.** Interpolated SST positive bias and total alkenones preserved in sediment resulting from selective degradation of alkenones in a 1G-RTM simulation assuming a rate constant ( $k_i$ ) of  $2.5 \cdot 10^{-5} \text{ year}^{-1}$ . (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth.  $\Delta SST$  denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}(0)$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C_{37:3}}$  denotes differential degradation factor between  $C_{37:3}$  and  $C_{37:2}$  alkenones.

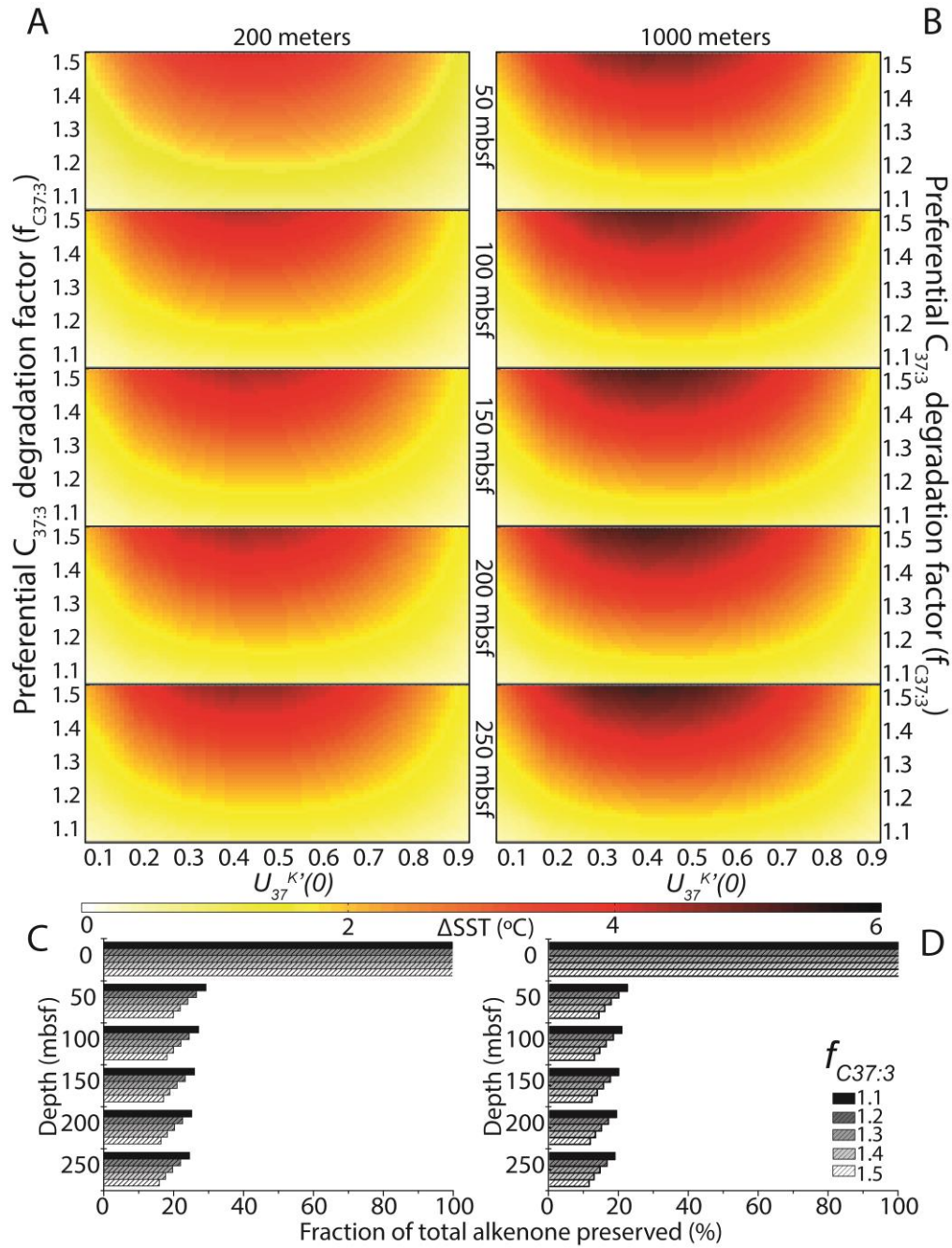




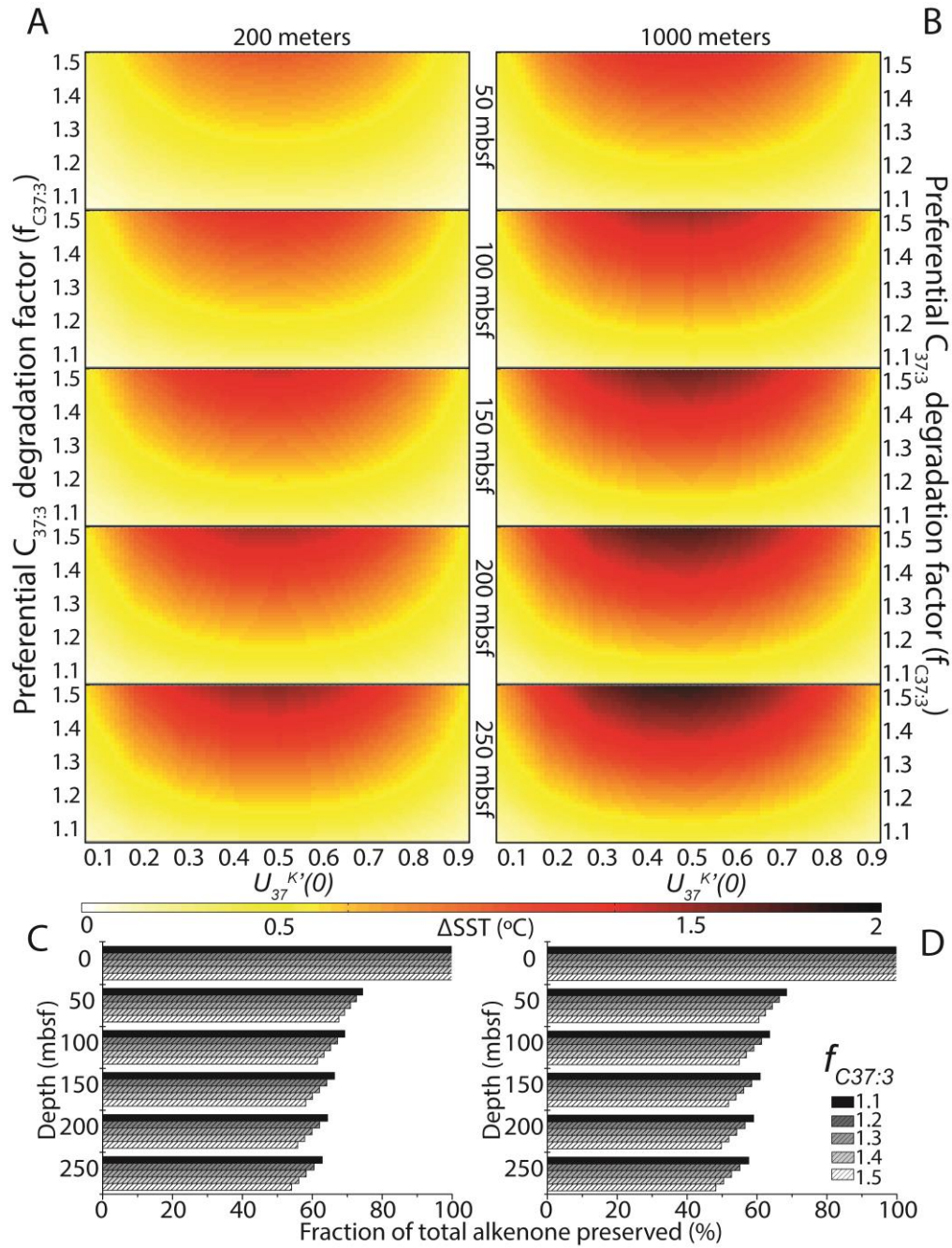
**Figure 5.** Interpolated SST positive bias and total alkenones preserved in sediment resulting from selective degradation of alkenones in a 1G-RTM simulation assuming a rate constant ( $k_i$ ) of  $5.0 \cdot 10^{-5} \text{ year}^{-1}$ . (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth.  $\Delta SST$  denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}(0)$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C_{37:3}}$  denotes differential degradation factor between  $C_{37:3}$  and  $C_{37:2}$  alkenones.



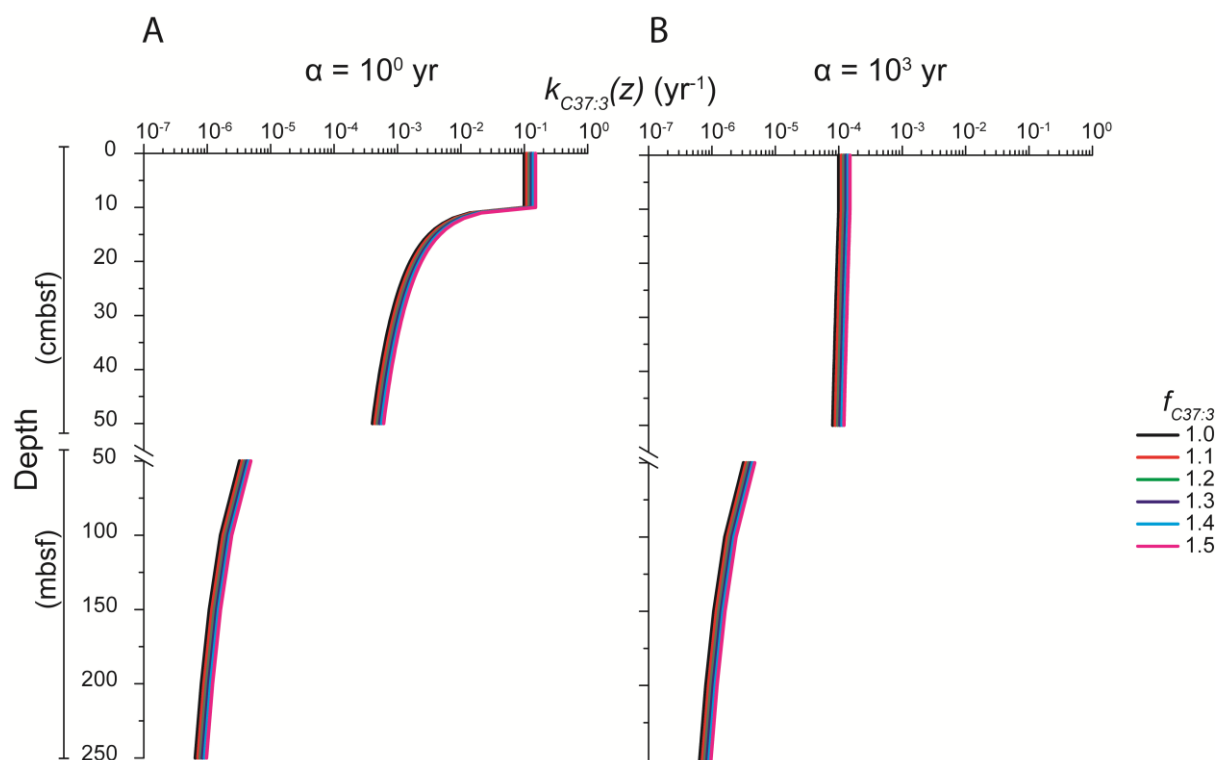
**Figure 6.** Interpolated SST positive bias interpolated plots and total alkenones preserved in sediment resulting from selective degradation of alkenones in a 1G-RTM simulation assuming a rate constant ( $k_i$ ) of  $1.0 \cdot 10^{-4} \text{ year}^{-1}$ . (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth. ΔSST denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C37:3}$  denotes differential degradation factor between C<sub>37:3</sub> and C<sub>37:2</sub> alkenones.



**Figure 7.** Interpolated SST positive bias and total alkenones preserved in sediment resulting from selective degradation of alkenones in a RCM simulation assuming  $pi = 10^{-1}$  and  $a_i = 10^0$  years. (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth.  $\Delta SST$  denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}(0)$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C_{37:3}}$  denotes differential degradation factor between  $C_{37:3}$  and  $C_{37:2}$  alkenones.

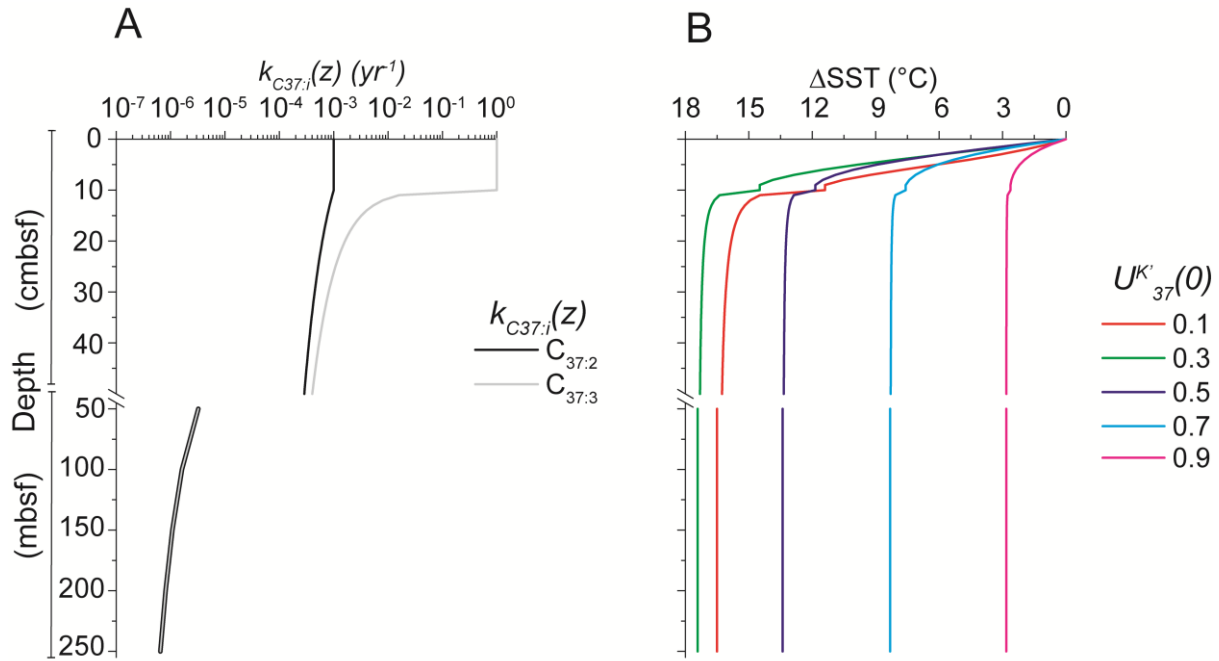


**Figure 8.** Interpolated SST positive bias and total alkenones preserved in sediment resulting from selective degradation of alkenones in a RCM simulation assuming  $pi = 10^{-1}$  and  $a_i = 10^3$  years. (a) Downcore SST bias at 200 meters water depth; (b) Downcore SST bias at 1,000 meters water depth; (c) Downcore total alkenones preserved (%) in sediment at 200 meters water depth; (d) Downcore total alkenones preserved (%) in sediment at 1,000 meters water depth.  $\Delta S_{ST}$  denotes SST at sediment-water interface (SWI) – SST at depth;  $U_{37}^{K'}(0)$  denotes  $U_{37}^{K'}$  initial values at SWI;  $f_{C_{37:3}}$  denotes differential degradation factor between  $C_{37:3}$  and  $C_{37:2}$  alkenones.

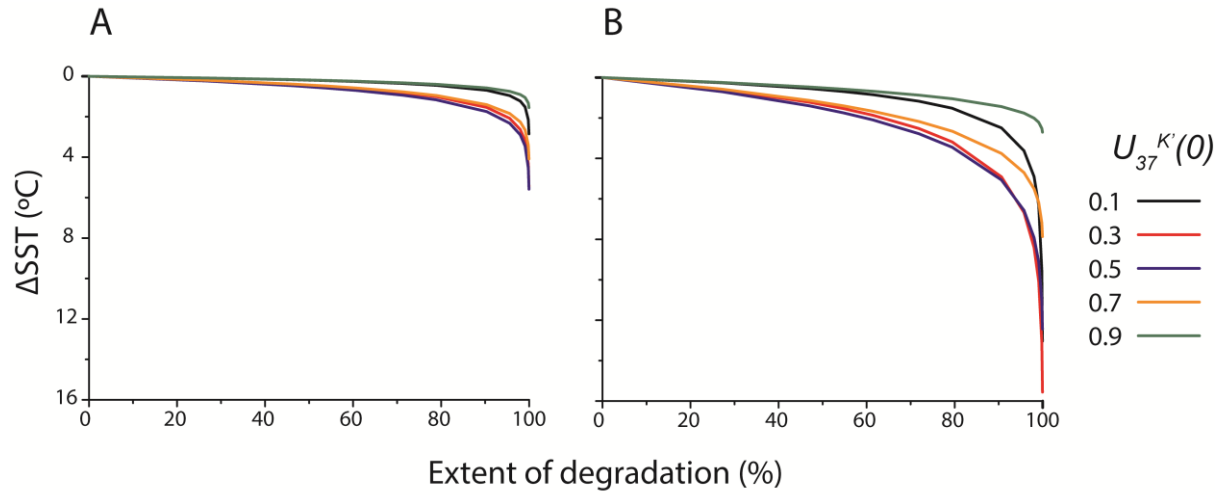


**Figure 9.** Simulated downcore changes in degradation rate constant  $k_{C37:3}(z)$  assuming:  $p_i = 0.1$ ;  $U_{37}^{K'}(0) = 0.5$ . (a)  $a_i = 10^0$  years; (b)  $a_i = 10^3$  years;  $f_{C37:3}$  ranges from 1.1 to 1.5 (colour lines); water depth = 1,000 meters. Note the break in scale at y-axis: top layers represent the top 50 cmbsf where the most significant changes in  $k_{C37:3}(z)$  and  $\Delta S_{ST}$  take place; below the break, bottom layers represent the deeper sediment layers > 50 mbsf. The discontinuity in the lines is due to the break in y-axis scale.

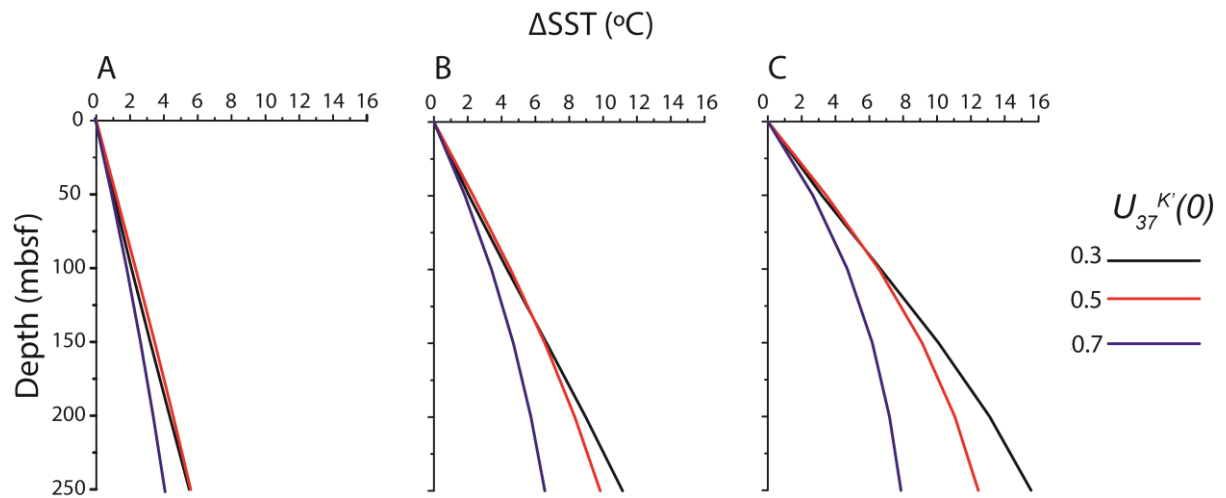




**Figure 10.** Simulated downcore changes in degradation rate constant  $k_{C37:i}(z)$  ( $C_{37:2}$  black line;  $C_{37:3}$  grey line) (a) and  $\Delta SST$  (b) applying a power model scenario assuming:  $pi = 0.1$ ;  $a_i = 100$  years for  $C_{37:2}$  (less labile pool of alkenones);  $a_i = 0.1$  years for  $C_{37:3}$  (more labile pool of alkenones);  $U_{37}^{K'}(0)$  ranging from 0.1 to 0.9 (colour lines in B); water depth = 1,000 meters. Note the break in scale at y-axis: top layers represent the top 50 cmbsf where the most significant changes in  $k_{C37:i}(z)$  and  $\Delta SST$  take place; below the break, bottom layers represent the deeper sediment layers > 50 mbsf. The discontinuity in the lines is due to the break in y-axis scale.



**Figure 11.** Increases in  $\Delta\text{SST}$  with an increase in the extent of  $\text{C}_{37}$  alkenone degradation. Simulations assume: (a)  $f_{\text{C}_{37:3}} = 1.1$ ; (b)  $f_{\text{C}_{37:3}} = 1.3$ . Line colours represent  $U_{37}^{K'}(0)$ : black = 0.1; red = 0.3; blue = 0.5; yellow = 0.7; red = 0.9.



**Figure 12.** Increases in  $\Delta\text{SST}$  with burial depth, assuming  $k_i = 5 \cdot 10^{-5} \text{ year}^{-1}$  and 1,000 meters water depth. (a)  $f_{\text{C}_{37:3}} = 1.1$ ; (b)  $f_{\text{C}_{37:3}} = 1.2$ ; (c)  $f_{\text{C}_{37:3}} = 1.3$ . Line colours represent  $U_{37}^{K'}(0)$ : black = 0.3; red = 0.5; blue = 0.7.

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